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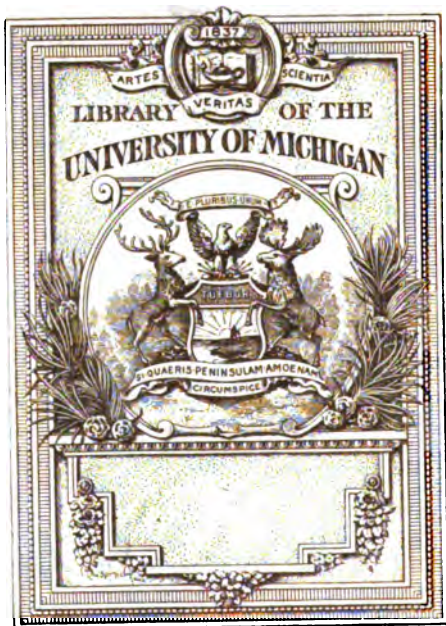
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INORGANIC  
GENERAL, MEDICAL AND PHARMACEUTICAL  
CHEMISTRY  
THEORETICAL AND PRACTICAL  
A TEXT-BOOK AND LABORATORY MANUAL

CONTAINING

THEORETICAL, DESCRIPTIVE, AND TECHNOLOGICAL CHEMISTRY; CLASS EXERCISES IN  
CHEMICAL EQUATIONS AND MATHEMATICS; AND PRACTICAL MANUFACTURING  
PROCESSES FOR FIVE HUNDRED CHEMICAL PREPARATIONS, WITH EXPLANATORY NOTES

BY

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*IN TWO VOLUMES*

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VOLUME I

1900

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## PREFACE.

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This book differs materially from the well-known treatises on general inorganic chemistry.

It was my chief aim in writing this book to prepare for the use of my own pupils a treatise on the pharmacy of inorganic chemistry, but this could not be accomplished without including in the book so much of general theoretical and descriptive chemistry that the inevitable outcome is instead a treatise on the inorganic chemistry of pharmacy including an adequate discussion of the fundamental principles of general theoretical chemistry. It would be as impossible to write a work on general inorganic chemistry without mentioning nearly all of the pharmaceutical chemicals as it is to write a treatise on special inorganic pharmaceutical chemistry without including in it all of the theoretical and descriptive chemistry necessarily belonging to a text-book on general chemistry. Practically all of the well-known, typical and most important inorganic chemical compounds are employed for medicinal and pharmaceutical as well as for industrial purposes. But while the text-books on general chemistry properly omit much of the matter that is essential to a treatise on chemical technology or on pharmaceutical chemistry, a reasonably complete work on pharmaceutical chemistry can not omit the general principles of the science.

Hence this book includes general theoretical chemistry, descriptive chemistry, the general principles and laboratory methods applicable to the production of inorganic chemicals, and practical exercises for the class room as well as the laboratory. It also includes manufacturing processes for five hundred important individual preparations.

In the treatment of the fundamental principles of theoretical chemistry I have sought to give the student clear conceptions of such important subjects as the atomic theory; chemical polarity; the relative intensity of the chemical energy of different elements; atomic valence; chemical notation and nomenclature;

the laws and conditions which dominate the course of chemical reactions; oxidation and reduction; the periodicity of the properties of the elements; the intimate relations of all these to each other and to atomic mass; and their bearings upon the practical problems of chemical work. Unimportant details, such as descriptions of rare, unstable and curious compounds having no use or general significance, and possessing no special interest to the students for whose use this book is intended, have been omitted, and especial attention given to basic principles and generalizations and to the inter-relations of fundamental facts. I have also included adequate instruction, rules, and examples, designed to enable the student to fully master the all-important practical uses of chemical equations and mathematics, seven chapters being devoted to these subjects.

The work is in accord with generally accepted chemical theories. Nothing contained in it is inconsistent with the teachings of Mendeléeff, Lothar Meyer, Ostwald, Ira Remsen, and other high authorities. Nevertheless there are some definitions and propositions in this book which may at first sight appear to be new because new in form. These appear in the summary of essentials of theoretical chemistry which constitutes Chapter XXVII; this chapter will serve to enable any one entitled to pass judgment upon contributions to our already large supply of chemical text-books to form a fair estimate of the general character of the whole work, except that the chapter referred to, being a recapitulation, does not contain examples, explanations and demonstrations given in the preceding twenty-six chapters.

The first chapter introduces the student to a number of common kinds of matter, such as air, water, earth, clay, sand, limestone, coal, metals, and various familiar oxides, acids, alkalies, and salts, which are described as fully as necessary to give the beginner some correct general conceptions of the composition of these substances to serve as a foundation upon which he may build his structure of technical knowledge. The second chapter treats of the divisibility of matter and gives definitions of such important technical terms as atom, molecule, chemism, and renders clear the differences between physical and chemical properties and changes, and the distinctions between elements, chemical compounds and mixed substances.

A sufficient number of practical experiments are then introduced illustrating chemical action and changes, and showing how chemical reactions are generally disclosed by the accompanying physical changes and phenomena.

After this elementary introduction to the nature of chemistry a brief general discussion of the chemical elements is entered upon, and the student's attention is called to the most striking physical and chemical differences between the pronouncedly metallic elements and the most characteristic non-metallic elements. In this discussion, as everywhere else, the student is led step by step, according to his capacity to grasp the subject with the aid of the preparation he has had in the preceding lessons.

The next chapter treats of the laws of definite combining proportions by weight and volume and the atomic theory, which are very fully described and illustrated by examples. Here, as in other places throughout the book, important definitions and doctrines have been repeated in different forms as far as deemed necessary to insure a true and full understanding of them.

Then follow the four chapters on Chemical Polarity, The Relative Intensity of the Chemical Energy of the Elements, Atomic Valence, and Atomic Polarity-Value.

Since chemists recognize the existence of the condition called chemical polarity by making use of such terms as "positive" and "negative" elements, radicals and ions, and our whole system of chemical notation and nomenclature may be readily seen to be based upon it, and as its reality is demonstrated by the Periodic System and by the obvious relations between polarity and valence, I have given that subject due attention.

The most practical use made of the doctrine of chemical polarity appears to be the method of balancing oxidation equations suggested by Professor Otis C. Johnson of the University of Michigan in 1880. I am indebted to him for the initiative to a further study of the bearings of this subject and for much of the material used in its elaboration.

Professor Johnson confined his application of chemical polarity to the employment of the terms "positive" and "negative" bonds in measuring oxidation and reduction. By the term "bond" he meant the unit by which oxidation is measured. He used the expression "oxidation-valence" which he defined

as the algebraic sum of the positive and negative bonds of any atom in combination, and warned against mistaking "oxidation bonds" for "structural bonds."

In this book, however, the term *bond*, wherever used, is employed only in its generally recognized sense. By bonds we mean "valencies" or units of valence. All bonds are structural bonds, and they are either positive or negative.

It is shown in this work that the true combining value of any atom in combination can be expressed only in terms referring to both polarity and valence. That value is designated by the author as *atomic polarity-value*, and it is assumed that the algebraic sum of the units of polarity-value of all atoms of all matter is always zero. The term "valence" is in this book used only in its generally accepted sense.

The descriptive chemistry in Vol. I is general in character and does not include processes of preparation of individual *compounds* which are fully treated in Vol. II.

Volume II of this work will take the place of Part II of the Laboratory Manual of Chemistry by Oldberg and Long, which is out of print. The great importance of laboratory practice in the production of chemical preparations is now so universally recognized that all technical schools where chemistry is taught include that kind of training. Manuals containing specific instructions for the preparation of a great variety of products are, therefore, necessary. The progress of the student as well as the work of the instructor must be exceedingly laborious without the aid of such a book. This manual includes probably all inorganic chemical preparations of medicinal or pharmaceutical use, and nearly all of commercial importance, together with many compounds introduced solely for purposes of instruction.

It is hoped that pharmacists and manufacturing chemists will find the working processes in Vol. II useful to them in their respective occupations.

Analytical processes are not treated of in this work.

In the work of proof-reading, my pupil, Mr. William L. Barnum, Jr., has rendered good assistance, which is hereby acknowledged.

OSCAR OLDBERG.

School of Pharmacy of Northwestern University,  
Chicago, 1900.

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PART I.

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ELEMENTARY  
THEORETICAL CHEMISTRY.



# ELEMENTARY THEORETICAL CHEMISTRY.

## CHAPTER I.

### INTRODUCTORY. — SOME COMMON KINDS OF MATTER.

1. Earth, air and water consist of *matter*.

The bodies of plants, animals and man are also composed of matter.

The sun, moon, and all other bodies in the universe, are, like our Earth and the bodies of and upon it, made up of matter.

2. **Matter** is that which occupies space and is affected by gravitation.

Thus matter has volume and weight.

Anything that has volume and anything that has weight is matter.

3. Matter occurs in three distinct **states of cohesion**: 1, the *solid*; 2, the *liquid*; and 3, the *gaseous* state.

All solids, liquids and gases are matter.

4. Matter is of innumerable kinds.

Each distinct kind of matter differs from any other distinct kind of matter by reason of its different composition or structure.

5. All kinds of matter may be classified into: 1, *elemental matter*; and 2, *compound matter*.

6. **Elemental matter** is matter which can not by any known means be decomposed into other kinds of matter, nor produced by combining together any other kinds of matter.

Elemental matter can not be transmuted into any other kind of matter.

7. Between seventy and eighty distinct kinds of elemental matter are known at this time (1900). They are called the **chemical elements**.

8. About three-fourths of the known elements are called *metals*; the others are called *non-metallic elements* (or "not-metals").

Aluminum, copper, gold, iron, lead, mercury, nickel, platinum, silver, tin and zinc are familiar examples of the metallic elements or metals.

Sulphur, carbon, phosphorus, bromine, iodine, are non-metallic elements; such are also the colorless gases, called oxygen and nitrogen, which make up the air.

9. All matter consists of indivisible and, therefore, undecomposable particles called *atoms*.

An **atom** is consequently the smallest particle of any element that can enter into the formation of any kind of compound matter.

10. There are as many distinct elements as there are different kinds of atoms.

About one-half of the nearly eighty distinct kinds of atoms at present known are of rare occurrence in nature; the others are more widely distributed and occur in larger quantities.

11. **Compound matter** is matter composed of two or more kinds of atoms, or of two or more elements, united together.

Compound matter can accordingly be decomposed into two or more other kinds of matter, and can be, directly or indirectly, composed out of, or produced by the union of, two or more other kinds of matter.

12. Each distinct kind of compound matter is called a **chemical compound**.

The number of distinct kinds of chemical compounds is countless.

13. Comparatively few chemical compounds exist in nature *in a pure condition*, or unmixed with other kinds of matter.

Nearly all pure or unmixed chemical compounds, then, are produced, or separated from other substances, by man's labor.

14. Examples of chemical compounds:

Water is a familiar chemical compound. It is composed of two elements, one called hydrogen and the other called oxygen.

Other familiar examples of chemical compounds are: common salt, alum, borax, green vitriol, blue vitriol, potash, baking soda, quartz, sugar, alcohol, glycerin, quinine sulphate, "carbonic acid gas."

Each of the chemical compounds is but one kind of matter, although composed of more than one kind of atoms and hence decomposable into other kinds of matter. Thus water is one distinct kind of matter decomposable into hydrogen and oxygen, each of which is another distinct kind of matter; and common salt is a distinct kind of matter decomposable into two other kinds of matter, one of which is called sodium and the other chlorine.

15. Nearly all substances, or bodies of matter, existing in nature consist of **mixtures** of two or more kinds of compound matter in varying proportions.

Earths, soils, wood, flesh, bone, oils, fats, resins, butter, milk, cheese, which may have the *appearance* of uniform composition, are nevertheless mixtures of chemical compounds, or are *mixed substances*.

16. **Inorganic substances** are those belonging to or derived from the mineral kingdom, as the rocks, earths, minerals, metals, the compounds formed by or containing metals, and, in fact, all kinds of matter not embraced in the definition of organic matter.

17. **Organic substances** are the kinds of matter peculiar to or derived from the bodies of plants or animals and composed of carbon and hydrogen together with other elements common to vegetable and animal substances, and also all other compounds formed by carbon and hydrogen with each other, and all derivatives of such compounds, and other related substances.

As examples of organic substances we may mention wood, flesh, blood, bone, white-of-egg, yolk-of-egg, milk, starch, sugar, cotton fibre, alcohol, benzin, glycerin, carbolic acid, camphor, coal oil, fats, quinine, acetic acid, wax, marsh gas, turpentine.

18. Water and air are held to be inorganic substances because they exist abundantly in nature independently of plants and animals. They are thus not of or from the bodies of plants and animals although they are contained in vegetable and animal tissues and organs as well as in minerals.

Water and air may, however, be looked upon as connecting media between plants, animals and earth, respectively, for reasons which will become apparent to the student later on in his study of chemistry.

19. **Air** is a mixture consisting almost wholly of two gaseous elements—nitrogen and oxygen. Both of these gases are color-

less and tasteless. They can not be compressed or condensed into liquids except under enormous pressure and with the aid of extreme cold; but liquid air is now produced, and if its production can be accomplished at moderate cost it might be extensively employed for various economic purposes.

Each five pounds of air contains about four pounds of nitrogen and one pound of oxygen.

Air also contains small and varying quantities of water in the form of vapor, and still smaller amounts of "carbon dioxide" or "carbonic acid gas." Carbon dioxide is a gas composed of carbon and oxygen.

Minute proportions of recently discovered gaseous elements are also contained in air.

Plants take up carbon dioxide from the air and exhale oxygen.

Animals inhale the air and appropriate a part of the oxygen; they exhale the unused part of the oxygen together with the nitrogen, and, with these, the carbon dioxide and water formed in the process of respiration.

**20. Oxygen** is that important constituent of the air which supports respiration and combustion, both of which are processes of oxidation.

*Oxidation* is a term which, in its narrowest sense, signifies the chemical union or combination of any other element with oxygen.

*Respiration* is attended with "slow combustion," by which certain substances contained in the venous blood entering the lungs are *oxidized* by the oxygen of the air inspired into these organs, and this process is a heat producing chemical action.

Slow oxidation may be seen not only in the results of respiration, but also in the tarnishing of iron and certain other metals when exposed to moist air.

*Fire* is a violent or rapid chemical process by which the burning substances, or one or more of their component elements, enter into combination with the oxygen of the air. This rapid oxidation is called *combustion* and produces heat, the intensity of this heat being in direct proportion to the rapidity of the oxidation.

**21. Oxides.** A compound formed by oxygen with any one other element is called an *oxide*.

All of the well known elements except fluorine form chemical compounds with oxygen.

Some of the elements have but one oxide each, or unite with

oxygen in only one proportion. Other elements unite with oxygen in two or more different proportions and thus have two or more different and distinct oxides.

The oxides are named, respectively, after the elements which form them by chemical combination with oxygen. Thus carbon united to oxygen forms an oxide of carbon; calcium combined with oxygen forms calcium oxide; silver oxide is a compound of silver with oxygen, etc.

22. To illustrate the formation of oxides by combustion in oxygen, or in air, the following examples are sufficient for our present purposes:

a. Sulphur burns with a blue flame combining with the oxygen of the air to form that oxide of sulphur which constitutes the very irritating colorless gas produced when sulphur matches are ignited. No ash is formed when sulphur undergoes combustion.

b. When charcoal, which is nearly pure carbon, is ignited and "consumed" by fire, or undergoes combustion, the carbon is oxidized. If the supply of air, or of oxygen, is insufficient, the product of the combustion of the carbon is, at least in part, an oxide which is composed of twelve parts of carbon and sixteen parts of oxygen. But, if the supply of air is abundant, another oxide is formed, instead, which is composed of twelve parts of carbon and thirty-two parts of oxygen. The latter oxide thus contains ~~nearly~~ twice as much oxygen as the former, in combination with the same quantity of carbon. Both oxides of carbon are colorless gases. *exactly.*

That carbon oxide which is composed of 12 parts of carbon and 16 parts of oxygen is *combustible*, burning with a blue flame when the supply of air is sufficient. It then takes up as much more oxygen as it contained before its ignition, forming the other oxide. That oxide which contains 32 parts of oxygen united to 12 parts of carbon is *not combustible* because carbon can not combine with more than  $2\frac{2}{3}$  times its own weight of oxygen.

When *pure* carbon is thus oxidized no ash is formed.

c. Alcohol is composed of the three elements carbon, hydrogen and oxygen. When it is ignited and burns in a free supply of air the flame is smokeless, no ash or residue is left, the products of the combustion of the alcohol being an oxide of carbon and an oxide of hydrogen (water).

d. Wood is a mixture of organic substances composed mainly of carbon, hydrogen and oxygen, but containing also some compounds of the elements potassium, calcium, silicon, etc. When wood is used as fuel the products of the combustion are chiefly the oxides of carbon and hydrogen which pass off with the smoke, while the compounds of potassium, calcium and silicon form the *ashes*.

e. When the soft, white metal called magnesium is ignited it burns very rapidly, emitting an intense white light, as it unites with the oxygen of the air to form a white solid which is magnesium oxide. The "flash-light" powder used by photographers consists of or contains powdered magnesium.

No gas is formed in the combustion of magnesium, for the only product is the oxide or oxygen compound of the metal, which is a fine powder, forming a cloud of white dust but no smoke. Five grams of this white ash or dust is produced by every three grams of the metal, because three grams of magnesium unites with two grams of oxygen. Hence when magnesium is said to be "consumed" by combustion it, in fact, yields a product, the weight of which is 66 per cent greater than that of the metal consumed.

f. When the black mineral called antimonite, which is a chemical compound formed by the elements antimony and sulphur, is strongly heated in the air ("roasted"), it decomposes; the metal antimony is oxidized to antimony oxide which fuses and forms a glass-like solid, while the sulphur combines with another portion of the oxygen of the air forming the gaseous sulphurous oxide which is produced by the burning of sulphur.

**23.** From these examples the student will learn that fire does not change the amount of matter in the world; it simply changes its composition and form.

Fire or combustion is one of the most striking of the numerous manifestations of chemical energy—that form of energy which determines any and all changes in the composition of matter.

**24. Water** is composed of hydrogen and oxygen. It is, therefore, an oxide of hydrogen.

Hydrogen and oxygen, at the ordinary temperatures, are both gases when not combined with each other or with other elements.

Water is one of the most wonderful substances in nature. It is the most neutral or indifferent substance, chemically, with regard to the vast majority of other kinds of matter, and accord-

ingly perfectly harmless when taken into the bodies of plants, animals and man. It forms solutions of numerous substances—solids, liquids and gases—and is indispensable to circulation and nutrition in all living organisms. It facilitates chemical processes without which life in the world of matter would be impossible.

**25. Acids.** Characteristic and comparatively “strong” acids, if water-soluble, have an acid or sour taste, and change the color of blue litmus to red.

Vinegar is acid or sour because it contains acetic acid.

Lemon juice is sour from citric acid.

Sour milk owes its sour taste to lactic acid.

Pie plant contains oxalic acid.

All acid or acidulous fruits contain some organic acid, or some acid compound formed by it.

Sour grapes are tart because they contain the compound called acid tartrate of potassium which is a salt formed by tartaric acid and which in its purified state is called cream of tartar, the sour taste of which is familiar.

Acetic, citric, lactic, oxalic and tartaric acid are all *organic acids* because they are acids derived from or contained in vegetable or in animal substances.

Many *inorganic acids* are also common. Among them are sulphuric acid, nitric acid, phosphoric acid, hydrochloric acid, and boric acid.

The student is probably somewhat acquainted with the impure, strong sulphuric acid formerly called “oil of vitriol,” the strong nitric acid formerly called “aqua fortis,” and the common strong hydrochloric acid popularly called “muriatic acid.” These strong inorganic acids are corrosive or destructive in their effects upon numerous other substances. They are, therefore, poisonous and dangerous, and should not be handled without great caution nor tasted except after great dilution with water.

Some acids are solids, others are liquids, and still others exist which are gases.

But *not all* acids are of acid taste, or corrosive, nor do all acids turn blue litmus red. Many acids are insoluble in water, and substances insoluble in water rarely have any taste. Insoluble acids are in no degree corrosive, nor do they affect litmus paper. They are nevertheless acids if their structure or composition and chemical behavior and the compounds they form are analogous

to those of the strongly characteristic acids, such as oxalic acid, sulphuric acid, or hydrochloric acid.

**26. Alkalies.** Caustic potash, caustic soda, and ammonia, are common commodities. They are the principal alkalies.

A solution of caustic potash in water is called "potash lye," and a solution of caustic soda is "soda lye."

Strong solutions of either caustic potash (the "potassa" of the Pharmacopoeia) or caustic soda (the "soda" of the Pharmacopoeia) are so destructive or corrosive that they "eat into" wood, dissolve flesh, and disintegrate bone. Strong ammonia solutions (called "water of ammonia," or simply "ammonia") also attack organic matter in a destructive way.

These alkalies have a burning, caustic, alkaline, lye-like taste; but their destructive character is such that they should not be tasted until after very great dilution with water.

They turn red litmus blue.

**27. Opposite properties of acids and alkalies.** While the strong acids and strong alkalies are alike destructive in their effects upon animal and vegetable tissues, they are nevertheless chemical opposites, for when an acid and an alkali are mixed together in certain definite proportions the corrosive or destructive properties of each are entirely taken away or neutralized.

We have seen that soluble acids turn blue litmus red and that the alkalies, on the contrary, turn red litmus blue. But when the acid and the alkali are mixed in proper proportions the mixture is one which does not affect either blue or red litmus.

To illustrate these facts let the student mix diluted hydrochloric acid and solution of soda.

The acid is very sour and promptly turns blue litmus paper red.

The soda solution is a lye and promptly turns red litmus paper blue.

If the acid be gradually added to the soda solution (the alkali), the mixture will, of course, continue to contain an excess of the alkali until a sufficient quantity of the acid has been added and the liquid will accordingly continue to turn red litmus blue for a time, but its effect upon the color of the litmus will become weaker and weaker until finally, when enough acid has been added, the litmus paper, whether red or blue, will not be altered in color by contact with the liquid. At the same time the alkaline

taste of the soda solution will diminish as the acid is added, and, when the mixture no longer changes the color of either blue or red litmus, the solution will be found not to have an alkaline taste, but, in its stead, a purely *salty* taste. In fact, when this point is reached, the liquid no longer contains any soda whatever, nor any hydrochloric acid, but is simply a solution of common *salt* (sodium chloride) in water, for the acid has completely neutralized the alkali, or the alkali and the acid have mutually wholly neutralized each other, and have formed a salt (and water) by chemical action or *reaction*.

If now the addition of more hydrochloric acid be continued the liquid begins to turn blue litmus paper red, because all of the alkali had been already neutralized and none of it remains to neutralize more acid so that the acid afterwards added must continue to be unneutralized or free hydrochloric acid.

**28. Bases.** A base (in inorganic chemistry) is a metallic oxide or hydroxide having the power to neutralize and form salts with acids.

The inorganic alkalies are, therefore, bases. But very few bases have decidedly alkaline properties.

Only the freely water-soluble metallic hydroxides and ammonia are called alkalies. A large number of inorganic bases are insoluble in water, tasteless, and apparently inert in their behavior toward most other substances except toward acids.

Some bases are solids, others are liquids, and others may be gases; but the metallic or inorganic bases are all solids.

**29. Basic properties and functions.** The characteristic properties of bases—i. e., their power to form salts with acids—are designated as *basic properties*.

The metals are said to exercise *basic functions*, or to be base-forming elements, because most of the oxides and hydroxides of the metals are bases.

**30. Acidic properties and functions.** The characteristic properties of acids—i. e., their power to form salts with bases—are designated as *acidic properties*.

The acids are, as a rule, compounds formed by non-metallic elements with hydrogen and oxygen (a few contain hydrogen without oxygen); but some of the metals also have the power to form acids.

Elements capable of forming acids are said to perform *acidic functions*, or to be *acid-forming elements*.

The most numerous class of inorganic acids is that of the hydroxyl acids, which are all composed of three elements, namely, hydrogen, oxygen, and the acid-forming element. Thus sulphuric acid is composed of hydrogen, oxygen and sulphur, the last named being the acid-forming element of sulphuric acid; carbon is the acid-forming element of carbonic acid; nitrogen is the acid-forming element of nitric acid; etc.

**31. Salts.** Salts are chemical compounds formed by acids with bases.

As the inorganic bases are oxides and hydroxides of the metals, it follows that the inorganic salts are also metallic compounds.

A metallic salt differs from an acid only in that the metallic salt contains a metal instead of the hydrogen of the acid, whereas an acid contains hydrogen in place of the metal of the salt. The acids are, accordingly, frequently referred to as the "salts of hydrogen."

**32.** The name "salt" belonged originally to the compound called sodium chloride, which is our common table salt. This salt is, as its name implies, composed of the metal sodium and the non-metallic element chlorine. Other solid substances made by early chemists were looked upon as other kinds of salts if they resembled sodium chloride in outward form or appearance, and especially if they were soluble in water. Thus boric acid, a white crystalline solid which forms borax when neutralized with sodium carbonate, was called "Sal Sedativum Hombergi;" benzoic acid, obtained in white crystals from benzoin, was called "Sal Benzoinum;" caustic potash, or potassium hydroxide, was sometimes called "Sal Tartari Causticum;" and other water-soluble homogeneous white solids received the name of "Sal," or salt, simply on the ground of the external resemblance between them and sodium chloride.

But scientific chemistry bases its classification and nomenclature of chemical compounds upon analogy or similarity of structure or composition instead of upon external form, appearance, and physical properties. Any compound having the structure proper to a *salt* is classed as such without regard to form, color, taste, solubility, and other physical properties.

**33.** As acids and bases mutually neutralize each other by

forming salts, so the salts thus formed may be decomposed again, and the acids and bases of which they were made may be reproduced or may be made to form other salts with other bases and acids.

**34.** Salts are named from the acids which produce them.

Thus all salts formed by hydrochloric acid are called chlorides; all salts formed by nitric acid are called nitrates, and those formed by nitrous acid are called nitrites; all salts formed by sulphuric acid are named sulphates, and the salts of sulphurous acid receive the name of sulphites; all salts formed by phosphoric acid are called phosphates; the salts of acetic acid are acetates; and the salts formed by citric acid are citrates.

**35.** As the acids can be reproduced out of their respective salts it follows that hydrochloric acid can be made from chlorides, nitric acid from nitrates, nitrous acid from nitrites, sulphuric acid from sulphates, sulphurous acid from sulphites, phosphoric acid from phosphates, acetic acid from acetates, citric acid from citrates, etc.

But many acids can be produced by other methods.

**36. Some common salts.** *Saltpetre* is a salt formed by nitric acid with the base called potassium hydroxide. It is, therefore, potassium nitrate. *Chili saltpetre* is sodium nitrate.

*Epsom salt* is formed by sulphuric acid with magnesium oxide (magnesia) or with magnesium hydroxide. It is the magnesium salt of sulphuric acid and is called magnesium sulphate.

*Washing soda*, or *Sal Sodae*, is sodium carbonate or the sodium salt of carbonic acid.

*Baking soda* is another sodium salt of carbonic acid called sodium bicarbonate or sodium "acid carbonate" because this salt contains in its molecule only one-half as much sodium as is contained in a molecule of the sodium carbonate which (in its crude or commercial form) is called washing soda.

*Green vitriol* is one of the iron salts of sulphuric acid, or a sulphate of iron; *white vitriol* is the sulphate of zinc; and *blue vitriol* is the copper salt of sulphuric acid or copper sulphate; but sulphuric acid is hydrogen sulphate or the sulphate of hydrogen.

**37.** Saltpetre, Epsom salt, washing soda, baking soda, the vitriols, alum, borax, and common salt have certain similarities of appearance and are all water-soluble solids. They are all really salts. But many other substances which *look like salts*

are not salts at all, as, for instance, boric acid, benzoic acid, oxalic acid, sodium hydroxide, potassium hydroxide, ice and snow, strychnine, rock candy, and numerous other compounds. On the other hand, glass, olive oil, chalk, clay, soap, oil of wintergreen, white lead, butter, and wax, although they bear no outward resemblance to common salt, or to saltpetre, or Epsom salt, or the vitriols, are really all of them salts, for they all have the structure of salts formed by acids with bases.

*Glass* is a mixture of the salts formed by silicic acid with the metals calcium, sodium, potassium and lead.

*Olive oil* consists chiefly of the salts formed by oleic acid and stearic acid with glyceryl, of which glycerin is the hydroxide.

*Chalk* is calcium carbonate, or the calcium salt of carbonic acid.

*Clay* is a salt of silicic acid with the metal aluminum.

*Soft soap* is chiefly the potassium salt of oleic acid, while *hard soap* consists of the sodium salts of oleic acid and stearic acid, both of which acids are obtained from the common animal and vegetable fats.

*Oil of wintergreen* is one of the salts of salicylic acid.

*White lead* is a carbonate of lead.

*Butter and wax* are mixtures of salts formed by certain peculiar "fat acids."

**38.** From the foregoing statements it is evident that salts may be either solids or liquids (and salts also exist which are gases); they may have various colors; they may be soluble or insoluble in water; and, in fact, may differ widely as to all of their physical properties.

**39. Earth.** The solid crust of the earth is made up mainly of rocks, clay, sand and other inorganic substances.

*Rocks* and clay are composed of salts.

*Sand* is an oxide of the non-metallic element called silicon.

Probably all elements enter into compounds which may be found contained in the earth's crust, or in waters on or under the earth's surface, or in the earth's atmosphere; but at least one element (helium) was discovered in the sun's spectrum before it was found to exist on the earth.

The most common and abundant elements contained in the substances which make up the crust of the earth are oxygen, silicon, calcium, carbon and aluminum.

40. *Limestone, chalk and marble* are different natural forms of calcium carbonate, composed of calcium, carbon and oxygen. When calcium carbonate is strongly heated it is decomposed into calcium oxide and carbon dioxide (one of the oxides of carbon).

*Lime* is calcium oxide. It is caustic and destructive to animal and vegetable tissues. When water is added to lime the mixture becomes so hot that steam rises, because chemical action takes place whereby the calcium oxide and the water together form calcium hydroxide composed of calcium, hydrogen and oxygen. Calcium hydroxide, or "slaked lime," is alkaline and turns red litmus blue.

*Carbon dioxide* is a colorless gas. When collected in water it "reacts" chemically with a definite proportion of the water whereby carbonic acid is formed. Carbon dioxide is, therefore, called "carbonic acid gas." Carbonic acid turns moist blue litmus red.

Now if lime (calcium oxide), or the slaked lime (calcium hydroxide), be exposed to the action of carbonic acid gas, we shall get calcium carbonate again, which does not change the color of either blue or red litmus.

41. Although calcium oxide and water may be said to unite to form calcium hydroxide, there is neither calcium oxide nor water in the calcium hydroxide formed; and although carbon dioxide and water unite to form carbonic acid there is neither carbon dioxide nor water in that acid. But calcium hydroxide can be decomposed into calcium oxide and water by simply heating the slaked lime, and when carbonic acid is heated it splits up into carbon dioxide and water.

To the beginner in the study of chemistry these statements will doubtless appear paradoxical; but there will be no difficulty in understanding them later on. For the present we will say that water is composed of two atoms of hydrogen and one atom of oxygen, the two hydrogen atoms being, both of them, united directly to the same oxygen atom; but in calcium hydroxide, and in carbonic acid, each oxygen atom, instead of being directly united to two hydrogen atoms, is united to only one atom of hydrogen. If calcium be represented by the symbol Ca, hydrogen by H, oxygen by O, and carbon by C, then the relative positions of the atoms composing calcium oxide, water, calcium hydroxide, carbon oxide, and carbonic acid, may be pictured as follows:

$\text{CaO}$ Calcium oxide.	$\text{HOH}$ Water.	$\text{HOCaOH}$ Calcium hydroxide.
$\text{OCO}$ Carbon dioxide.	$\text{HOH}$ Water.	$\begin{array}{c} \text{O} \\ \text{HOCO} \end{array}$ Carbonic acid.

**42.** When any stronger acid, as sulphuric acid, hydrochloric acid, or even acetic acid, is added to calcium carbonate, this salt is decomposed and "carbonic acid gas," or carbon dioxide, is given off with effervescence. If sulphuric acid be added to marble, calcium sulphate and carbonic acid are formed; if hydrochloric acid be used instead of sulphuric acid, the products will be calcium chloride and carbonic acid, and if acetic acid be mixed with the marble we shall get calcium acetate and carbonic acid.

**43.** Carbon is familiar in the several forms of hard coal, soft coal, charcoal, black lead, and diamond.

The student has read in this chapter that when carbon undergoes combustion in a full supply of air it combines with the oxygen of the air to form a colorless gas which is an oxide of carbon. That oxide is the same (carbon dioxide) as that obtained when calcium carbonate is decomposed by strongly heating it, or when a stronger acid is added to calcium carbonate, or when carbonic acid is decomposed.

**44.** The radical changes which matter may undergo through chemical action are already strikingly illustrated by the examples given. We will now repeat a few of these illustrations in another way and add others:

Sulphur is a yellow, odorless solid; carbon is, in its ordinary forms, a black, odorless solid; iodine is a purplish black solid having a strong characteristic odor; mercury is a silver-white, heavy liquid of brilliant metallic lustre; bromine is a brown-red, heavy liquid of powerful, penetrating and highly irritating odor; hydrogen, oxygen and nitrogen are all colorless, odorless and tasteless gases; and chlorine is a greenish gas of strong, irritating odor. But sulphur forms one oxide which is an irritating, colorless gas, and another oxide which is a white odorless solid, although, containing a larger proportion of the gaseous element, oxygen, than the gaseous oxide. The odorless solid elements, carbon and sulphur, form an odorous liquid compound called carbon disulphide. The liquid mercury forms a solid red or yel-

low oxide and another solid black oxide. Carbon and hydrogen form with each other many different compounds, some of which are gases, other liquids, and still others solids. The compounds formed by hydrogen with chlorine, bromine and iodine are colorless acid gases. But hydrogen, nitrogen and chlorine, all of which are gases, unite to form a white odorless solid called ammonium chloride. Hydrogen and nitrogen, both odorless gases, form the gas called ammonia which has a strong, suffocating odor. And the two odorless and colorless gases, nitrogen and oxygen, form with each other several compounds which are gases or liquids; colorless, blue or red; odorless, or of extremely irritating odor.

The foregoing examples illustrate **chemical changes** or **reactions** and **chemical composition**.

**45.** If the student has read this chapter carefully he must now know at least something about several important elements and compounds. This knowledge, although very limited, will aid the student in making further progress, for the substances already described will serve as familiar objects with which many future lessons may be readily connected.

**46. Chemistry** is the science of the composition and structure of matter.

It accordingly takes cognizance of the divisibility and relative stability of molecules and of their composition and decomposition.

## CHAPTER II.

### ATOMS, MOLECULES AND CHEMISM.

**47. The divisibility of matter.** Chemistry, as at present taught and practiced, rests upon the hypothesis that the divisibility of matter is not limitless.

The existence of absolutely indivisible and, therefore, undecomposable particles of matter called *atoms* is universally recognized.

All matter is composed of atoms.

**48.** The chemical *elements* are substances consisting of but one kind of atoms.

As nearly eighty kinds of atoms are at present known, there are nearly eighty known chemical elements.

All the different kinds of matter so far examined have been found to be composed of one or more of that limited number of atoms.

But it is highly probable that still other kinds of atoms exist which may yet be discovered.

**49.** All atoms of the same kind have the same mass, and are alike as to all their properties.

**50.** Atoms rarely exist singly or uncombined with other atoms. They are almost invariably found combined with each other into atomic groups consisting of two or more atoms of one kind or of different kinds.

**51. Chemism.** That form of energy by which atoms are attracted to each other and linked or held together in groups is called *chemical energy*. It is also called chemism, or chemical attraction, or chemical affinity, atomic attraction, or chemical combining energy.

This force or form of energy appears as if inherent in every atom.

**52.** All chemical changes are changes in the composition or structure of matter, and all such changes are the manifestations and results of chemical energy or chemism.

As the formation, transformation, and decomposition of different kinds of matter thus depend upon chemism, the preserva-

tion of each kind of matter, or its resistance to change, must also be subject to the power of chemism or chemical energy. The relative stability of different kinds of matter is, therefore, one of the chief concerns of the science of chemistry, and the means by which the constitution of matter may be determined.

53. Our conceptions of energy and motion are always associated with our conception of matter, for energy is that which causes motion, and the idea of motion is inseparable from the idea of that which is moved, and that which is moved is matter.

One of the "general properties of matter" is *inertia*—the inability of matter to move without the impulse of some force (energy) external to itself, and its inability of its own accord to stop its motion when once started.

Energy manifests itself in two opposite modes—*attraction* and *repulsion*.

Distinction is made between different forms of attraction and repulsion, respectively, according to the conditions and results.

The attraction which operates between all separate bodies of matter in the universe is called *universal gravitation*; the ruling power by which the earth attracts toward its center other bodies of lesser mass is a result of gravitation and is called *weight*.

The attraction operating between molecules is called *molecular attraction*; the term *adhesion* signifies attraction between molecules of different kinds, while attraction between molecules of any one kind is called *cohesion*.

Attraction operating between atoms is, as we have already seen, called *chemism*. But chemical energy is probably, like electricity (and magnetism), a polar force, for it causes mutual attraction only between atoms of opposite polarities, respectively, and probably mutual repulsion between atoms having respectively the same polarity. (See Chapter VI.)

Heat acts in opposition to both molecular attraction and atomic attraction. Electricity also opposes atomic attraction.

Heat, light and electricity are distinct modes of molecular motion, while chemical action is atomic motion; but molecular motion may cause, or interfere with, or be converted into, atomic motion; and atomic motion may cause, or affect, or be converted into molecular motion. Energy of any kind can be changed into energy of any other kind. Thus the different "forces" which act upon matter are only different forms of one universal energy.

Whenever energy of one kind disappears its exact equivalent in another form appears in its place. The transmutability of chemical energy into other forms of energy, such as heat, light, electricity, and even mechanical energy, is of the first importance in the economy of nature and an everyday experience.

54. But as all forms of energy are interconvertible, and as molecular attraction and motion must affect and be affected by atomic attraction and motion, the student should learn from the start to avoid confusion between them.

We have said that *adhesion* is that form of molecular attraction by which molecules of different kinds are mutually attracted to each other. The unlike molecules thus mutually attracting each other may be held together with greater or less force, and in definite or indefinite proportions. But the composition of each distinct chemical compound depends upon *chemical energy* and its laws.

*Mixtures* may be made in any proportions; yet, many compound substances are known which apparently *consist of distinct unlike molecules in definite proportions*, and, as these combinations thus resemble chemical compounds in that they are *of definite composition*, they are generally classed with the true chemical compounds. It is, however, extremely important that a clear distinction be made between *combinations of molecules* and *combinations of atoms*.

55. Chemical energy is *potential* when unused, as in free or uncombined atoms.

*Actual* chemical energy is that energy by which any atom holds one or more other atoms in combination with itself.

56. Chemical energy may be studied with regard to its *quality* called chemical polarity, its *intensity*, and its *quantity*.

Atoms of different kinds may exhibit wide differences in respect to the quality, intensity and quantity of the chemical energy which actuates them, and these differences depend upon various conditions. The *quality* of the chemical energy of hydrogen is the very opposite of the quality of the chemism of oxygen. (See Chapter VI.)

The *intensity* of the chemical energy of fluorine is so great that it can not be held in an uncombined state, while the newly discovered element, argon, shows no tendency to combine with any other element. (See Chapter VII.)

The *quantity* of the chemical energy required to produce any given chemical combination may not be *directly* measured; but chemical energy may be made to pass into thermal energy and as any given quantity of energy of any kind always produces a definite corresponding quantity of energy of any one other kind, it follows that chemical energy when transformed into heat may be *indirectly* measured in thermal units—the units in which heat is measured.

Chemical energy causes *atomic motion*; thermal energy causes that kind of *molecular motion* which is called heat. Whenever any two or more elements unite to form a chemical (atomic) compound, a certain amount of chemical motion is converted into heat motion; when the same compound is decomposed again into its elements, exactly the same quantity of heat is required to cause the decomposition as that liberated when the compound was formed.

But elemental molecules nearly always consist of more than one atom and then must be split up into atoms before the atoms can form compound molecules; a certain amount of energy is required to separate the like atoms of the elemental molecule from each other, and hence the *heat of formation* of compounds can only represent the *difference* between the energy required to separate the atoms of the elemental molecules and the energy required to form the new compound. Moreover, thermal energy is *absorbed* when solids form liquids or gases, or when liquids form gaseous compounds, and the *evolution* of thermal energy results when gases form liquids, or when liquids or gases form solid compounds. These facts must be remembered in connection with the interpretation of the stated results of the inter-conversion of chemical energy and heat.

When 207 Gm. of lead and 254 Gm. of iodine are united to form 461 Gm. of lead iodide the quantity of heat liberated by the reaction is equivalent to that required to raise the temperature of 39,800 grams of water  $1^{\circ}$  C. Lead, iodine, and lead iodide are all solids.

When 127 Gm. of solid iodine and 1 Gm. of gaseous hydrogen form gaseous hydriodic acid, the reaction is accompanied by *absorption* of heat amounting to 6,100 calories (sufficient heat to raise the temperature of 6,100 Gm. of water  $1^{\circ}$  C.); but the

gaseous hydriodic acid dissolves in water with the evolution of 19,200 calories.

**57.** Another important feature of chemical combining power concerns the relative saturating capacity of each individual atom. This is called *valence*. One atom of oxygen can hold in combination two atoms of hydrogen, but an atom of chlorine can hold in combination with itself only one atom of hydrogen.

The intensity of the chemical energy actuating each atom is generally sufficient to cause all atoms to combine with other atoms, so that free atoms, or atoms existing alone or uncombined, are rare exceptions.

It is, however, sometimes found, when atoms of two or more different kinds are combined with each other, that the combining power of one of these elements is but partially used, and the proportion of the combining power actually occupied or used is in any such case one or more aliquot parts of the whole measure of the potential atomic combining capacity of the element not wholly saturated. Such atoms have a variable valence. (See Chapter VIII.)

**58. Radicals.** Any atom or group of united atoms capable of taking part in the formation of a molecule, or actually entering into a molecule, is, for the sake of convenience, called a radical.

Every single atom is a radical because in its free or uncombined state it possesses *potential* chemical combining power by means of which it can enter into combination with other radicals, and when combined with any other atom or atoms it exercises *actual* combining power.

A group of united atoms possesses *potential* chemical combining power if one of the elements of that group still retains unused combining capacity by means of which the whole group may become united to other atoms or groups of atoms, and when such a group of united atoms takes part in the formation of a molecule it exercises *actual* combining power.

As one atom of oxygen has the power to hold two atoms of hydrogen in combination with itself, an atomic group consisting of one oxygen atom and one hydrogen atom is a radical since the combining power of the oxygen is only one-half used or occupied, and this radical has the power to combine with any other radical of opposite quality of combining energy.

Radicals are incapable of continued independent existence except in solutions (Chapter VI.).

**59.** Single atoms are *elemental radicals*.

Groups of united atoms of two or more kinds acting together in the formation of molecules are called *compound radicals*.

The group consisting of one oxygen atom and one hydrogen atom united to each other is, therefore, a compound radical, and this compound radical, which occurs in numerous chemical compounds, is called *hydroxyl*.

**60.** **Molecules** are the smallest particles of matter which are capable of separate or independent continued existence, or subsistence.

They may consist of one or more atoms; but molecules consisting of single atoms (monatomic molecules) are extremely rare.

**61.** All kinds of matter are made up of molecules, and these, in turn, are made up of atoms.

**62.** **Elemental molecules** are molecules consisting of but one kind of atoms. The chemical elements, or the several kinds of elemental matter, consist of elemental molecules

**63.** **Compound molecules**, or *chemical compounds*, are molecules composed of more than one kind of atoms, or of two or more elements.

**Every compound molecule is formed by one, and only one, complete and independent system of atomic linking.**

Compound matter is matter consisting of compound molecules of but one kind.

**64.** **Mixed substances**, or *mixtures*, consist of molecules of more than one kind, mixed together in proportions independent of chemical laws.

**65.** Molecules consisting of but one atom are called *monatomic molecules*; those containing two atoms are *diatomic molecules*; molecules composed of three atoms are called *triatomic molecules*; *tetramolecular molecules* contain four atoms; *pentatomic molecules* are made up of five, and *hexatomic molecules* of six atoms.

Molecules containing many atoms are said to be *poly-atomic*.

Compound molecules containing many hundreds of atoms are supposed to exist.

**66.** As all molecules consist of atoms it follows that all mole-

cules may be regarded as formed by the combination of radicals.

The atoms of all molecules consisting of more than two kinds of atoms may, either singly or in groups, or both singly and in groups, be recognized as the radicals out of which the molecules are formed.

**67.** While it is assumed that atoms rarely subsist singly or uncombined, or, in other words, continue to remain single or free for any period of time (except as ions in solutions), it is obvious that changes of matter from one kind to another would be impossible were it not for the separation of the atoms of existing molecules and the rearrangements of the same atoms into new molecules. The atoms must be released from existing combinations before they can enter into new combinations. They can be transferred, either singly or in groups, from one molecule to another, and at the moment of such transfer they must be regarded as radicals endowed with potential chemical combining power.

**68.** All the atoms in any compound radical act together as one radical, or as if the whole group were but one atom.

Compound radicals may, therefore, unite with each other as elemental radicals do, and, like single atoms, they may be transferred without change from one molecule to another.

**69. Saturated molecules** are molecules in which the chemical combining power of each and every atom is completely satisfied, occupied, or exhausted.

Saturated molecules, therefore, have, as such, no potential chemical combining power and are incapable of entering into true chemical combination with each other, or with any atoms or groups of atoms.

**70.** Many combinations between molecules are known, but they are not chemical compounds in the same sense as compound molecules (atomic compounds). Molecules of one kind may form combinations in definite proportions with molecules of another kind, but such **molecular combinations** are not chemical compounds because they are not the results of atomic linking in accordance with the laws of polarity and valence, but of some form of molecular attraction which is not yet understood.

**71. Unsaturated molecules** are molecules in which one of the component atoms still possesses additional, or unused, or potential chemical combining power whereby the whole molecule may be united to another atom or atomic group.

The molecule of carbon monoxide is an unsaturated molecule because it is composed of one atom of carbon united to only one atom of oxygen, whereas one carbon atom can hold in combination two atoms of oxygen, so that the combining power of the carbon atom in the monoxide is only one-half satisfied, and the carbon monoxide can combine with another oxygen atom to form the saturated molecule called carbon dioxide, while at the same time the *carbon monoxide exists as an independent kind of matter.*

Unsaturated molecules generally exhibit a tendency to enter into chemical combinations whereby they form other and saturated molecules.

Unsaturated molecules are all of them radicals; but only those radicals are unsaturated molecules which are capable of at least temporary independent existence. Other radicals are not molecules.

**72.** All monatomic molecules are unsaturated. Zinc, cadmium, mercury and iodine are known to exist in monatomic elemental molecules at high temperatures, and one or two of the recently discovered gaseous elements contained in the uncombined state in the air are believed to consist of monatomic molecules at ordinary temperatures.

**73.** All molecules of the same kind have the same volume and mass and the same properties in all respects.

Each molecule of any particular chemical compound invariably contains the same kinds of atoms, the same total number of atoms, and the same number of each kind of atoms; and all the atoms of one molecule occupy the same positions relative to each other as those of any other molecule of the same compound.

**74.** There are as many different kinds of matter, elemental and compound, as there are different kinds of molecules—no more and no less.

Every new kind of matter must consist of a new kind of molecules.

**75.** *Chemically homogeneous substances* are distinct kinds of matter consisting of but one kind of molecules, whether elemental or compound.

All chemically homogeneous substances are also physically homogeneous.

**76.** *Physically homogeneous substances* are substances of uni-

form appearance and apparently uniform physical properties. Such a substance may consist of but one kind of matter, elemental or compound; but many physically homogeneous substances as, for instance, solutions, alloys, benzin, volatile oils, fixed oils, and air, are mixtures of two or more kinds of molecules although each such mixture *appears* externally to be of perfect sameness throughout its whole mass.

77. Distinction must be made between the terms "physical mixture" and "chemical mixture." All physical mixtures are, of course, also chemical mixtures, but a substance which, chemically considered, is a mixture of several kinds of molecules may be an unmixed natural product and, therefore, can not be called a physical mixture, as, for instance, olive oil, lard, oil of lemon, tolu balsam, and wheat flour.

78. The **physical properties** of matter are those properties which can be discovered by means not involving any alteration in the composition or structure of its molecules, or, in other words, by other than chemical means. The physical properties of matter are extra-molecular, or belong to any number of its molecules taken together. They include form or state of cohesion or aggregation, crystalline form, specific weight, color, odor, taste, solubility, melting point, boiling point, etc.

But while the physical properties of matter may be discovered and determined without any reference to chemistry, they nevertheless depend primarily upon the composition and structure of the molecules.

79. The **chemical properties** are those properties of matter which can not be discovered or determined without reference to its composition and structure. They depend directly and exclusively upon intramolecular conditions and include the masses and the intensity, polarity and valence of the combining power of the atoms of which the molecules are composed, and the composition, structure (interatomic linking), mass, reactions and relative stability of those molecules. (See Chapter VIII.)

80. **Matter is indestructible.** The quantity of matter in the universe is a fixed quantity. It can neither be added to nor diminished.

The changes to which any kind of matter may be subject are, therefore, not changes of mass, but changes of position, structure and properties.

81. All the properties, physical and chemical, of each distinct kind of matter, or, in other words, of any one kind of molecules, are invariably the same under the same conditions.

82. *Allotropy*. Certain elemental substances seem to occur in different forms, the properties of each distinct form or modification differing materially from those of the other form or forms of the same element. This occurrence of one element in several distinct forms, each having materially different properties, is called *allotropy*, and the several distinct forms which the element assumes are called its *allotropic modifications*.

Carbon, sulphur, phosphorus and several other elements exist in strikingly different allotropic modifications. Diamond, graphite and charcoal are all carbon; sulphur occurs in at least four distinct modifications which differ in form, consistence, color, solubility, and other particulars; phosphorus occurs as a waxy, white solid and also as red powder.

The causes of allotropic modifications are not understood.

Diamond and graphite doubtless both consist exclusively of carbon atoms, but their molecules must evidently be differently constituted or associated, for it is inconceivable that they could otherwise possess such essentially different properties. Possibly the number of atoms of carbon contained in each molecule of the diamond may be different from the number of atoms in each molecule of the carbon that constitutes graphite and the kind of carbon called charcoal; or perhaps these different forms of carbon differ by reason of differences in the arrangement of the atoms in the respective molecules; or it may be that the several allotropic modifications result from differences in both the number and the grouping of the atoms. That elemental molecules of gases may vary according to conditions as to the number of atoms they contain has been proven. The number of atoms contained in the molecules of solids can not as yet be determined.

But the differences between the several allotropic modifications of any element may perhaps be accompanied or caused by differences of intermolecular structure or differences in the relative arrangement of their molecules, instead of differing interatomic or intramolecular conditions.

83. No two different kinds of matter have exactly the same physical properties in every particular.

Any two masses of matter having exactly the same physical properties in every particular must, therefore, be of one kind.

**84.** Any substance may undergo a change of properties, or a change of kind, or both, when subjected to changed conditions.

A partial change of the physical properties of any substance may take place without any change in its chemical composition.

**85.** A change in any one or more of the physical properties of any substance unaccompanied by any alteration in its chemical structure is a purely *physical change*, and such physical changes are always due to changes in the physical conditions to which the substance is exposed, such as changes of temperature or pressure, contact or intermixture with other substances, etc.

When water is frozen to ice this change is a physical or extra-molecular change, and the conversion of water into steam is equally a physical alteration, for the water, ice and steam all consist of the same kind of molecules—the molecules of hydrogen hydroxide (or hydrogen oxide, as generally regarded).

**86.** A *chemical change* is a change of chemical composition and structure (interatomic linking).

Whenever any substance undergoes a chemical change its very identity is lost, and it becomes another kind, or two or more other kinds, of matter. Its own distinctive molecules disappear and new and different molecules take their place.

Thus when water is decomposed into its elements, hydrogen and oxygen, this change is a chemical change because the molecules of hydrogen hydroxide cease to exist and molecules of hydrogen and molecules of oxygen take their place.

Chemical changes are always attended by physical changes.

**87.** As the physical properties of any given kind of matter are the same under the same or unchanged conditions, it follows that changes of the physical properties of matter *generally* denote chemical changes as their causation, although purely physical changes (without accompanying chemical change), due to molecular forces, are not uncommon.

Among the physical changes which always prove that chemical changes are their causes we may mention changes of color, odor, taste, reaction on test-paper, volatility, fusing point, and density, when such changes are unaccompanied by changes of external physical conditions.

## CHAPTER III.

### EXPERIMENTS SHOWING PHYSICAL SIGNS OF CHEMICAL ACTION.

Whenever any particular substance loses any one of its physical properties, such as color, odor, taste, density, melting point, boiling point, or solubility, it has ceased to be that substance.

Whenever any two substances are brought into contact with each other and any chemical reaction or reactions occur therefrom, the physical properties of the substances thus brought together disappear, and the physical properties of the new product or products appear instead. Sometimes the physical phenomena accompanying chemical reactions are striking enough to command attention; but in other cases they escape observation.

A few experiments are here presented to illustrate and exemplify the foregoing statements:

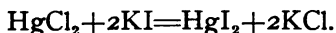
**Exp. 1.**—Strike a friction-match. The friction produces heat. This heat causes the ingredients of the composition on the end of the match to react upon each other and with the oxygen of the air. This reaction intensifies the heat motion. The products of the reaction are gases; hence the noise. The gases are inflammable and are ignited by the heat of the reaction. Flame, therefore, appears. The wood of the match becomes heated until it begins to undergo chemical decomposition, and the gaseous products of that decomposition (or chemical reaction) also burn with a flame. The substances of which the match was made have completely disappeared and have given place to invisible gases, which are scattered in the air, and small quantities of charcoal and ash, which remain.

**Exp. 2.**—Put 0.50 Gm. of potassium chlorate and 0.50 Gm. of sulphur in a mortar and triturate the two substances together. A series of explosions will occur producing a smattering noise caused by chemical reaction between the salt and the sulphur, the products being gaseous.

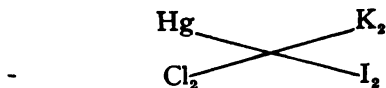
**Exp. 3.**—Put a few crystals of chromic acid upon a piece of paper; put about thirty or forty drops of strong alcohol into a

test-tube, and then pour that alcohol out of the test-tube upon the crystals. Observe the commotion which takes place. The chromic acid is reduced to chromic oxide by losing one-half of its oxygen, and the alcohol is oxidized to acetic acid; but the heat produced by the chemical reaction vaporizes another portion of the alcohol and ignites the vapor so that fulmination results.

**Exp. 4.**—Mix 400 milligrams of corrosive sublimate and 500 milligrams of potassium iodide in a white mortar. Both of the materials put together are white; but the mixture will become scarlet red because the mercuric chloride (corrosive sublimate) and the potassium iodide have ceased to exist by reacting upon each other, the products of the interaction being potassium chloride (which is white) and mercuric iodide which is of a deep scarlet red color. The reaction is represented by the following equation:



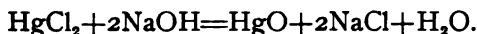
Mercury (Hg) and potassium (K) are both metals. When mercury unites with two atoms of chlorine ( $\text{Cl}_2$ ), the compound formed by these two elements is mercuric chloride ( $\text{HgCl}_2$ ). When potassium unites with iodine (I), the compound formed is potassium iodide (KI). But when mercuric chloride and potassium iodide meet, the two metals change partners; the potassium takes the chlorine from the mercuric chloride, and the mercury unites with the iodine of the potassium, thus—



When the corrosive sublimate and potassium iodide are mixed dry the chemical reaction between them is slow and incomplete; but if some water is added the change is rapid as well as complete.

**Exp. 5.**—Mix in a white mortar 1 Gm. of mercuric chloride ( $\text{HgCl}_2$ ) and 0.40 Gm. of sodium hydroxide ( $\text{NaOH}$ ). The materials are both white, but the mixture will be yellow, because the molecules of  $\text{HgCl}_2$  and  $\text{NaOH}$  disappear and new molecules take their place which are yellow mercuric oxide

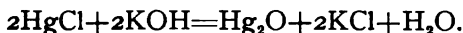
(HgO), white sodium chloride (NaCl), and colorless water (H<sub>2</sub>O). The reaction is thus represented—



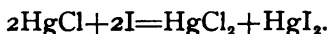
If the materials are dry the reaction is slow and incomplete; but the addition of water makes the reaction both rapid and complete.

Mercuric chloride has a very disagreeable persistent metallic, acrid taste; but as it is very poisonous the student should not taste it in any other way than by merely touching first the chloride and then his tongue with the moistened end of his finger. Sodium hydroxide ("caustic soda") is extremely corrosive, and hence should not be tasted without great caution; when it is touched with the wetted end of the finger and the latter dipped in water and then applied to the tongue, the taste will be found to be alkaline. But when mercuric chloride and sodium hydroxide have mutually decomposed each other, the new products are the nearly tasteless (slightly metallic) mercury oxide, common table salt, and water. The student may taste the mixture in the mortar; but he should, of course, in this as in all cases, when poisons, corrosive or other potent substances are tasted, be careful not to swallow any of it.

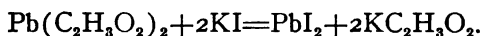
**Exp. 6.**—Mix 1 Gm. of calomel (mercurous chloride) and 1 Gm. of potassium hydroxide in a white mortar. The materials are white, but the mixture will be grayish black, and the change takes place more quickly if a little water be added. The blackish product is mercurous oxide—



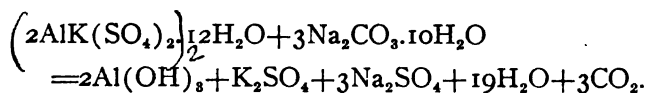
**Exp. 7.**—Mix 1 Gm. of calomel (HgCl) and 1 Gm. of iodine in a white porcelain mortar. The calomel or mercurous chloride is white and the iodine is purplish-black. The iodine, moreover, has a characteristic strong odor. Triturate the two substances together until the mixture assumes a bright red color and becomes odorless. The mixture now contains mercuric iodide which renders it bright red, and the odor of the iodine is no longer detected because that element has entered into chemical combination with the mercury. The mixture also contains mercuric chloride.



**Exp. 8.**—Mix 0.90 Gm. of lead acetate and 0.80 Gm. of potassium iodide in a white mortar. The materials are white; the lead acetate has a disagreeable, sweetish, astringent, metallic taste, and the potassium iodide has a disagreeable, pungent, saline taste. The mixture becomes light yellow from tasteless, yellow lead iodide, the by-product being white potassium acetate having a not disagreeable saline taste. The reaction is—



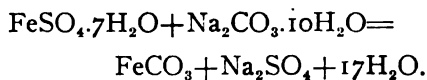
**Exp. 9.**—Mix 1 Gm. of crystallized alum and 1 Gm. crystallized sodium carbonate. Both materials consist of hard, transparent, colorless crystals. These are to be crushed to powder and triturated together. The mixture becomes quite wet from the water of crystallization liberated when the salts react upon each other, thus—



Alum has a sweetish astringent taste and the sodium carbonate an alkaline taste; but the mixture of the products formed from them is neither astringent nor alkaline but bitter and saline in taste.

[Equal parts of lead acetate and alum, when triturated together, also react upon each other, liberating water which renders the mixture wet.]

**Exp. 10.**—Mix 5 Gm. of ferrous sulphate and 5 Gm. of sodium carbonate in a dry mortar. Ferrous sulphate consists of pale green crystals, and sodium carbonate of colorless crystals; both are hard, dry solids. The mixture will be *wet*, first grayish-white, then gray, then brownish and finally yellowish-red. The water which wets the mixture comes from the water of crystallization contained in the salts constituting the “factors of the reaction,” which is thus shown—



But the ferrous carbonate ( $\text{FeCO}_3$ ) at once begins to decompose. Effervescence accordingly occurs from the escape of

$\text{CO}_2$ , and the ferrous compound is changed to ferric by oxidation from the oxygen in the air, and the color changes as the proportion of ferric compound increases.

If *dried* ferrous sulphate and *dried* sodium carbonate be mixed there will be scarcely any chemical reaction between them; but when water is added the reaction at once begins.

Ferrous sulphate and sodium carbonate are both water-soluble; but iron carbonate is insoluble and the basic ferric hydroxide resulting from its decomposition in contact with the air and water is also insoluble.

Ferrous sulphate has an inky or chalybeate taste, and sodium carbonate an alkaline taste; but the products of the "double decomposition" which takes place between them are one of them tasteless (because insoluble) and the other bitter and saline.

**Exp. 11.**—Put 34 Gm. of diluted sulphuric acid (10 per cent strength) into a beaker. Dip the end of a glass rod in it, touch that to the end of your tongue and observe how acid it tastes. A little strip of blue litmus paper turns red when touched with the acid.

Add 5 Gm. of potassium carbonate gradually to the diluted acid; but before adding it take a very minute quantity into your mouth so as to observe its strong alkaline taste. A strip of moist red litmus paper turns blue when touched with the potassium carbonate.

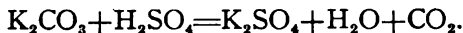
When you add the carbonate to the acid in the beaker be careful to add it in small portions at a time, stir well after each addition, and wait until effervescence has subsided before adding more. The effervescence is a sign that a chemical reaction is taking place. Also observe that the mixture becomes warm, which is another evidence of chemical action.

When all of the potassium carbonate has been added and effervescence has ceased, taste the liquid; it is now neither acid nor alkaline, but saline and bitterish. It does not turn blue litmus paper red, nor red litmus paper blue if the proportions of acid and alkali were right.

Should the liquid turn red litmus paper blue it contains potassium carbonate which was used "in excess"; in that case, add a little more diluted sulphuric acid, very gradually, until the liquid becomes perfectly neutral to both red and blue litmus paper. Should the liquid turn blue litmus red it contains an

excess of acid; in that event add a little more potassium carbonate, very cautiously, until a perfectly neutral reaction on test-paper is insured.

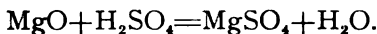
The chemical reaction in this case is represented by the following "equation"—



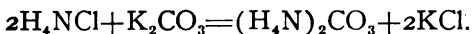
The effervescence is caused by the escape of the  $\text{CO}_2$ , which is a gas ("carbonic acid gas").

The rise in the temperature of the liquid as the reaction progresses is a common result of the saturation of acids by alkalies or alkali carbonates.

**Exp. 12.**—Touch a little dilute sulphuric acid (on the end of a glass rod) to your tongue and observe its strongly acid taste. Taste a little magnesia and notice that it is almost tasteless. Now put 10 ml. of diluted sulphuric acid into a beaker, and add gradually 5 Gm. of magnesium oxide (magnesia), stirring the mixture with a glass rod. When the liquid no longer dissolves any more of the white powder, taste it; it has a bitter, saline, cooling taste, for it contains no more sulphuric acid but magnesium sulphate (Epsom salt) instead—

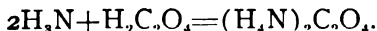


**Exp. 13.**—Observe that potassium carbonate has no odor, and that ammonium chloride, too, is odorless. Mix 5 Gm. of each of these salts in a mortar and observe the strong ammoniacal *odor* developed. They react upon each other as follows—

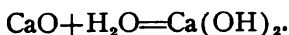


**Exp. 14.**—Observe the strongly acid taste of oxalic acid, and the acrid alkaline taste and stifling pungent odor of ammonia water. Also note that oxalic acid in solution turns blue litmus paper red, and that ammonia turns the reddened paper blue again.

Add 2 Gm. of oxalic acid to 5.4 Gm. of ammonia water (of 10 per cent strength) and 15 Gm. of water. The solution is *odorless* and has a saline taste instead of an acid or alkaline one. It contains neither oxalic acid nor ammonia, but ammonium oxalate which does not affect litmus paper—



**Exp. 15.**—Put 8 Gm. of calcium oxide (quicklime) in a dish and pour over it 5 Gm. of water. Observe how the lime absorbs the water, crackles, becomes so heated that a portion of the water forms steam, and the lime finally falls to powder. The calcium oxide unites chemically with the water forming calcium hydroxide (slaked lime)—

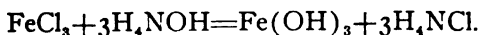


**Exp. 16.**—Dissolve about 0.10 Gm. of blue vitriol (copper sulphate) in 20 ml. of water, and observe that the color of the solution is pale blue. Add a few drops of ammonia water and see how the color deepens. Add a little more ammonia water and dilute the liquid with water as long as the blue color may still be distinctly seen.

This experiment shows not only a chemical change by the change of color, but it also illustrates the extreme divisibility of matter and the intensity of color which may be produced by extremely dilute solutions of some substances. These effects are also seen in the next experiment.

**Exp. 17.**—Dissolve 0.01 Gm. of sodium salicylate in 100 ml. of water, and observe that the liquid is colorless. It contains only 1 part of the salt in 10,000 parts of water. Now add a few drops of tincture of chloride of iron and observe the "color reaction" produced. Then add gradually enough diluted hydrochloric acid to "discharge" the reddish or purplish color and render the liquid colorless again. The successive color changes are due to chemical reactions.

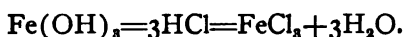
**Exp. 18.**—Put about 5 ml. of the pharmacopœial solution of ferric chloride in a beaker (or in an Erlenmeyer flask) and dilute it with 25 ml. of water. Observe the reddish-brown color of the solution. Add 5 ml. of ammonia water and mix well. Observe that a brown-red "precipitate" is formed and that the mixture has no ammoniacal odor. Now add another 2 ml. of ammonia water; more precipitate will be formed and the mixture will acquire the odor of ammonia.



The brown-red precipitate is ferric hydroxide  $[\text{Fe}(\text{OH})_3]$  and the liquid contains ammonium chloride  $[\text{H}_4\text{NCl}]$  in solution to-

gether with the small quantity of ammonium hydroxide  $[H_4NOH]$  added in excess of the amount required to decompose the ferric chloride  $[FeCl_3]$ .

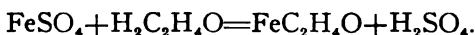
Finally add enough hydrochloric acid to redissolve the precipitate; the acid  $[HCl]$  reacts with the precipitated ferric hydroxide  $[Fe(OH)_3]$ , forming ferric chloride again and water:



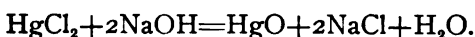
Compare the result of the addition of ammonia to the iron solution in the first part of this experiment with the result obtained in the next experiment (Exp. 19) where the same substances are mixed in the same manner and proportions but where sugar is dissolved in the iron solution before the ammonia is added.

**Exp. 19.**—Put 5 ml. of official solution of ferric chloride into an Erlenmeyer flask, add 10 Gm. of white sugar and 20 ml. of water. When the sugar shall have been dissolved, add 7 ml. of ammonia water. No precipitate will be formed in this case, but the color of the iron solution becomes deeper. In the absence of sugar a precipitate of ferric hydroxide would be formed (as in Exp. 18), but with sugar present a water-soluble ferric compound is produced containing sugar and some ammonia.

**Exp. 20.**—Dissolve 2 Gm. of pure green vitriol (ferrous sulphate) in 20 ml. of water, and 2 Gm. of oxalic acid in another 20 ml. of water. Mix the two solutions and observe that a yellow "precipitate" is slowly formed. A "double decomposition" has taken place whereby the ferrous sulphate and oxalic acid have given place to ferrous oxalate and sulphuric acid—



**Exp. 21.**—Dissolve 5 Gm. of mercuric chloride in 100 ml. of hot water. Dissolve 2 Gm. of sodium hydroxide in 50 ml. of water; observe that the water in which the sodium hydroxide is dissolved becomes warm from the condensation going on as the sodium hydroxide attracts a part of the water. Now add the solution of mercuric chloride slowly to the other solution, stirring well. Note that a precipitate having a rich orange-yellow color is formed; this precipitate is mercuric oxide.



Compare this experiment with Exp. 5 and Exp. 22.

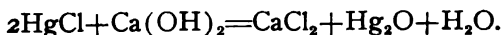
**Exp. 22.**—Dissolve 5 Gm. of mercuric chloride in 100 ml. of hot water, and 2 Gm. of sodium hydroxide in 50 ml. of cold water, precisely as in Experiment 21. But instead of adding the solution of mercuric chloride to the “alkali” solution, reverse the order of mixing—pour the solution of sodium hydroxide *slowly* into the solution of mercuric chloride; observe that the color of the precipitate is *not* now a clean orange yellow, but instead a dirty-brown. Why this difference? Because in Exp. 21 the mercuric oxide first formed was produced in a liquid containing an excess of sodium hydroxide, by which the mercuric oxide is not affected; but in Exp. 22 the mercuric oxide first produced comes in contact with an excess of mercuric chloride, with which it combines to form an oxychloride—a compound of mercury with oxygen and chlorine, instead of pure mercuric oxide. The amount of mercuric oxychloride formed is not definite. The precipitate is lighter in color when the proportion of oxychloride in it is small, and darker when the proportion of oxychloride in it is greater.

Let the dirty-colored oxychloride of mercury sink to the bottom of the flask; pour off the “supernatant liquid,” and then pour upon the wet oxychloride a sufficient amount of official solution of NaOH or of KOH to cover it, shake well and let the mixture stand a little while. The brown oxychloride now changes to orange-yellow oxide, because a considerable excess of alkali decomposes the oxychloride, removing the chlorine from it.

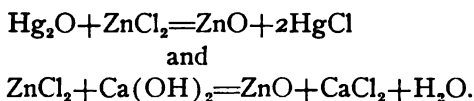
**Exp. 23.**—Put 10 Gm. of potassium bicarbonate in a porcelain dish and add enough water to cover it. Apply heat. Effervescence takes place. When effervescence has ceased evaporate the liquid to dryness. Observe that the potassium bicarbonate was crystallized, not hygroscopic, and not very freely soluble in water; but the residue after heating is not capable of forming large crystals and is hygroscopic and extremely readily soluble in water.

$2\text{KHCO}_3$  is decomposed by heat into  $\text{K}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$ .

**Exp. 24.**—Put 0.50 Gm. of calomel in a bottle, add 100 ml. of limewater and shake well. Observe that the calomel, which is insoluble, turns nearly black, just as in Exp. 5. It is converted into black mercurous oxide by the calcium hydroxide contained in the limewater.



Now add 0.50 Gm. of zinc chloride to the mixture in the bottle, and set it aside, shaking it occasionally. After some time the nearly black color of the insoluble powder in the bottle changes to white, for it becomes a mixture of calomel and zinc oxide:

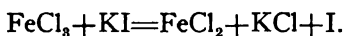


Compare the results with those of Exp. 25.

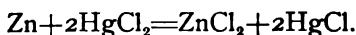
**Exp. 25.**—Put 0.50 Gm. of zinc chloride in a bottle with 100 ml. of limewater, and shake well. Observe that a white precipitate or insoluble powder is formed. Now add 0.50 Gm. of calomel and shake thoroughly. Observe that the insoluble matter remains white. The calomel is *not* changed to mercurous oxide; but the zinc chloride reacts with the calcium hydroxide to form zinc oxide, calcium chloride and water.

Compare this with Exp. 24.

**Exp. 26.**—Put 0.50 Gm. of potassium iodide in a bottle and add 10 ml. of water; then add 2 ml. of tincture of chloride of iron. Observe that the mixture becomes dark and unclear from iodine which is liberated and which may be easily identified by its odor:



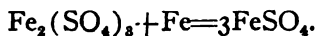
**Exp. 27.**—Put 5 Gm. of mercuric chloride into a bottle with 100 ml. of water, and heat until the chloride is completely dissolved. Then add 0.50 Gm. of zinc filings and digest for an hour, shaking frequently. The zinc will all dissolve and calomel will take its place.



**Exp. 28.**—Put 0.50 Gm. of copper sulphate and 100 ml. of water in a bottle, and add 1 ml. of diluted sulphuric acid. When the blue vitriol has been completely dissolved insert a bright nail or other piece of clean iron into the liquid and leave it there until coated with metallic copper. A portion of the iron dissolves, tak-

ing the place of an equivalent proportion of copper which is deposited upon the undissolved portion of the iron.

**Exp. 29.**—Put 10 ml. of solution of ferric sulphate (U. S. P.) into a bottle with 10 ml. of water. Add 0.5 Gm. of iron wire or iron filings and digest until the reddish-brown color of the liquid is changed to pale green. The iron reduces the ferric sulphate to ferrous sulphate.



## CHAPTER IV.

### THE CHEMICAL ELEMENTS.

**88.** The elements may, with great advantage, be divided into two classes: 1, the *metals*; and 2, the *non-metallic elements*.

Of the 74 elements here enumerated 57 are *physically* metals and 17 are non-metals.

*The physically metallic elements are:*

#### VERY IMPORTANT.

Aluminum.  
Antimony.  
Arsenic.  
Bismuth.  
Calcium.  
Copper.  
Gold.  
Iron.  
Lead.  
Magnesium.  
Mercury.  
Potassium.  
Silver.  
Sodium.  
Tin.  
Zinc.

#### LESS IMPORTANT.

Barium.  
Cadmium.  
Cerium.  
Chromium.  
Cobaltum.  
Iridium.  
Lithium.  
Manganese.  
Molybdenum.  
Nickel.  
Platinum.  
Strontium.  
Tungsten.

#### COMPARATIVELY RARE.

Beryllium (or Glucinum).  
Cæsium.  
Columbium.  
Erbium.  
Gallium.  
Germanium.  
Indium.  
Lanthanum.  
Neodymium.  
Osmium.  
Palladium.  
Præscodymium.  
Rhodium.  
Rubidium.  
Ruthenium.  
Samarium.  
Scandium.  
Tantalum.  
Tellurium.  
Terbium.  
Thallium.  
Thorium.  
Titanium.  
Uranium.  
Vanadium.  
Ytterbium.  
Yttrium.  
Zirconium.

*The non-metallic elements are:*

#### IMPORTANT.

Boron.  
Bromine.  
Carbon.  
Chlorine.  
Fluorine.  
Hydrogen.  
Iodine.  
Nitrogen.  
Oxygen.  
Phosphorus.  
Sulphur.  
Silicon.

#### RARE.

Argon.  
Crypton.  
Helium.  
Neon.  
Selenium.

### 89. Differences between the metals and the non-metallic elements.

It is impossible to draw the line absolutely between metallic and non-metallic elements, for several elements partake more or less of the characteristics of both classes, physically and chemically.

Hydrogen, which is a gas and, therefore, possesses none of the physical properties of metals (unless at so low a temperature and under such enormous pressure as have not yet been applied to it) is unmistakably most closely related to the metallic elements in its chemistry.

The following comparisons will be found helpful to the student:

#### PHYSICALLY METALLIC ELEMENTS.

#### NON-METALLIC ELEMENTS.

##### *State of Cohesion at Ordinary Temperatures.*

The metals are solid with the sole exception of mercury, which is a liquid.

Of the 17 non-metallic elements boron, carbon, iodine, phosphorus, selenium, silicon and sulphur (7) are solids; bromine (1) is liquid; argon, chlorine, crypton, fluorine, helium, hydrogen, neon, nitrogen and oxygen (9) are gases.

##### *Tenacity, Ductility and Malleability.*

Most of the metals exhibit one or more of these properties in a greater or less degree.

But there are many metals which are not tenacious, ductile or malleable. Among these are antimony, arsenic, chromium, manganese, molybdenum, tungsten, vanadium and zinc, all of which resemble the non-metallic elements more or less in their chemical behavior (being capable of performing "acidic functions").

Not one of the non-metallic elements possesses any one of these properties.

##### *Specific Weights.*

Only 15 of the 57 metals have specific weights below 5.

The five alkali metals range in density from 0.6 to 1.5; the five alkaline earth metals from 1.6 to 4. The specific weights of the other metals range from 5.5 to 22.42.

In other words the metals are generally *heavy*.

The specific weights of all the non-metallic elements are below 5. The densities of six of them are lower than that of any metal; and only carbon, selenium and iodine have densities exceeding 3.

*Atomic Weights.*

Only 5 metals have atomic weights below 36. They are lithium, beryllium, sodium, magnesium and aluminum.

Only 3 non-metallic elements have atomic weights exceeding 36. They are selenium, bromine and iodine.

*Color.*

In compact masses the metals have usually a white color with a more or less marked tendency toward grayish, bluish, or reddish; but barium and calcium are yellowish, gold is yellow, and copper is reddish. Bismuth in crystalline masses displays variegated hues of purplish with its reddish white.

The non-metallic elements in solid form differ decidedly from the metals in appearance, and they also differ much from each other in that respect.

Boron is black. Carbon is either black (as in coal and graphite) or perfectly colorless (as in diamond). Iodine is purplish black. Phosphorus is commonly of a light yellowish waxy translucent appearance, but perfectly white when pure; and in another form that element is of a dull, dark-red color. Selenium is either red or black. Silicon is brown or gray. Sulphur is pale yellow, amber, dark brown, or nearly milk-white, according to its condition or allotropic modification. Hydrogen, oxygen, nitrogen, argon, helium, krypton and neon are colorless gases. Chlorine is a greenish gas. Fluorine is a greenish-yellow gas. Bromine is a brown-red liquid.

*Lustre.*

All the metals possess a peculiar ("metallic") lustre. This lustre is in many instances greatly heightened by polishing. But some of the metals have a rather dim lustre.

All the solid non-metallic elements, in some form, possess a kind of lustre; but not the "metallic lustre," except that carbon in the form of graphite has a metallic lustrous appearance. The lustre of crystallized iodine approaches that of the metals. The lustre of the diamond differs entirely from and far exceeds that of any metal.

*Fusibility.*

All metals are fusible; some of them at temperatures below the boiling point of water, others only at extremely high heat (exceeding 1,000 deg.). But the greatest number melt between these extremes of temperature.

Of the solid non-metallic elements carbon, boron and silicon are infusible. Sulphur, selenium, phosphorus and iodine are fusible, and these fuse at comparatively low temperatures.

### *Volatility.*

Of the metals only mercury, potassium, sodium, magnesium, zinc, cadmium and arsenic can be readily distilled; antimony and tellurium can be distilled with a current of hydrogen.

Iodine, phosphorus, selenium, sulphur and bromine are readily vaporizable.

### *Conductivity.*

Metals are relatively better conductors of heat and electricity than the non-metallic elements. But some metals possess this property in a much higher degree than others, and those metals which are good conductors when in solid, compact masses are poor conductors when in a state of fine powder (as obtained by precipitation and in certain other ways).

Non-metallic elements are non-conductors or poor conductors of heat and electricity.

### *Solubility in Common Solvents.*

All metals are absolutely insoluble in water, alcohol, ether, chloroform, glycerin, the liquid hydrocarbons, carbon disulphide, volatile oils and fixed oils.

The non-metallic elements are nearly all insoluble in water. Chlorine, bromine and iodine dissolve in water to a very small but still appreciable extent.

Iodine is soluble in alcohol, glycerin, chloroform, liquid hydrocarbons, carbon disulphide, volatile oils and fixed oils.

Phosphorus is soluble in chloroform, ether, absolute alcohol, carbon disulphide and fixed oils.

Sulphur is soluble in chloroform, benzin, carbon disulphide, oil of turpentine, and fixed oils.

### *Compounds.*

Some metals are capable of combining *with each other* in definite proportions, sometimes forming even crystallizable compounds. But such compounds are comparatively rare and *decidedly metallic in all their properties*. They are "molecular compounds."

The metals can also be fused together to form physically homogeneous mixtures, which are *not* molecular compounds (although they may *contain* such). All combinations of metals with each other, obtained by fusing them together, whether they be or con-

The compounds formed by non-metallic elements with other non-metallic elements and with the metals are countless, and they rarely in any respect or degree resemble their component elements or either of them in their properties.

*Compounds—Continued.*

tain definite compounds or not, are called *alloys*, and their physical properties are in no case essentially different from those of single metals. They retain in a high degree the metallic characteristics of their constituents or ingredients. (Brass, bronze, gun-metal, bell-metal, German silver, type metal, pewter, Britannia metal, and solder are examples of alloys.)

Alloys containing mercury are called *amalgams* and some of these are liquid; but all other alloys are solid, hard, tenacious, ductile, malleable, lustrous, or brittle, as the case may be, according to the character of their constituent metals. Their color, too, is such as would naturally result from physical intermixture rather than chemical union.

Some metals form *alloys* with *hydrogen*; but elements which are truly metals in the chemical sense do not unite with hydrogen to form *chemical compounds*.

Tellurium, arsenic and antimony, however, combine with hydrogen. They are, therefore, only physically, and not chemically, metals.

All metals form chemical compounds with *oxygen*, called "oxides." The metallic oxides, *as a rule*, form "salts" with the compounds called "acids." Many of these oxides when brought in contact with moist reddened litmus paper change the color of the paper to blue. But the higher oxides of a few metals are "acidic oxides."

The most characteristic metals form compounds with hydrogen and oxygen together, called hydroxides, which do not unite with each other, but which are capable of neutralizing acids (taking away their acid properties), and the properties of metallic hydroxides are, therefore, opposite to the properties of acids.

All the well-known non-metallic elements form chemical compounds with hydrogen.

The oxides of non-metallic elements never form salts with the acids. Many of these oxides turn moistened blue litmus paper red; no such oxide turns red litmus paper blue.

Most of the non-metallic elements form compounds with hydrogen and oxygen together, which compounds are acids. The acids never combine with or neutralize each other, but they do saturate or neutralize the properties of the metallic hydroxides, of which they are the opposites.

Metallic hydroxides capable of neutralizing acids are called "bases," and when bases and acids mutually neutralize each other the resulting products are water and salts. The metals, therefore, generally perform a *basic function* in the formation of salts. A few metals, however, do perform acidic functions in some of their compounds.

All acids contain hydrogen. That hydrogen is called the basic hydrogen of the acid. Metals are capable of replacing the basic hydrogen of acids, and whenever a metal takes the place of the basic hydrogen of an acid the acid is thereby changed to a salt.

When a metallic compound is decomposed by an electric current, the metal is always liberated at the negative electrode and the metals are accordingly said to be of *positive polarity*.

Hydrogen is invariably of positive chemical polarity in all its compounds, and when liberated from any of its compounds in electrolysis it passes to the negative electrode. The metallic elements being like hydrogen in that respect, can take the place of hydrogen in compounds. Hydrogen is, therefore, sometimes referred to as "the gaseous metal."

The non-metallic elements do not perform basic functions in the formation of salts. They are, instead, acid-formers, or perform *acidic functions*.

Chemically non-metallic elements can not replace the basic hydrogen of acids and thus form salts.

When a compound formed by a metal with one or more non-metallic elements is subjected to electrolysis (decomposed by an electric current), the non-metallic element (or the compound radical composed of non-metallic elements) is liberated at the positive electrode. Hence the non-metallic elements (hydrogen excepted) are said to be of *negative polarity* in relation to the metals.

Oxygen is invariably of negative polarity in all its compounds. It is in fact the only element except fluorine having an invariably negative chemical polarity.

Other non-metallic elements, except hydrogen alone, are sometimes negative and sometimes positive, but their ruling polarity is negative. Thus while they are always positive in relation to oxygen they are always negative in relation to hydrogen and the metals.

90. The majority of the metals possess invariably all the characteristics mentioned in the preceding pages, and stand in sharp contrast opposite the pronouncedly non-metallic elements.

Most of the non-metallic elements are equally readily recognized as in no way partaking of the characteristic physical or chemical properties of metals.

But there are several elements which, as indicated, have the physical properties of metals but the chemical behavior of non-

metallic elements; and there are other elements, having metallic lustre and otherwise resembling the metals in their physical properties, which, in *some* of their compounds, are analogous to the decidedly pronounced metals and in *other* compounds act like the most decidedly non-metallic elements.

91. From the purely chemical point of view all elements which form compounds analogous to those of hydrogen, which can replace basic hydrogen but do not form interatomic combinations directly with that element (or with hydrogen alone), and which form basic oxides, can be placed together in one class which would include all of the most characteristic metals.

92. The elements which combine directly with hydrogen (or can form compounds by direct atomic linking with hydrogen alone without the intervention of any third element), which can *not replace* basic hydrogen, and which form only acidic oxides, can be placed together in another class which would then include the most characteristic non-metallic elements.

93. Hydrogen, which is the only invariably positive non-metallic element, and oxygen, which is an invariably negative element, could not be placed in either of the two classes just referred to, but the vast importance of these two elements in the realm of matter, and their singularly peculiar properties and functions in chemistry, have always rendered it necessary that they be studied before the chemistry of any other elements can be intelligently approached, and it seems probable that this will always be the case.

94. Elements which in some of their compounds perform functions analogous to those of decidedly metallic elements, and in other compounds the functions of decidedly non-metallic elements, occupy, chemically, an intermediate position between metals and non-metals, not only in respect to the compounds they form, but also as to their relative positions in the natural groups and series resulting from an arrangement of the elements in the order of their atomic weights and the periodicity of their chemical relationships, as will be shown in the Chapter XXVI. on The Periodic System.

95. The following example of elements which partake of the properties of both metals and non-metals are sufficient to emphasize in a particular way what has already been stated in general terms:

*Antimony* is a heavy metal of decided lustre, but its oxides are

generally acidic (forming antimonates and antimonites), although its acidic functions are feeble. It stands chemically on the border line between the metals and the non-metals.

*Arsenic*, when not tarnished by exposure, exhibits metallic lustre and is heavy; yet it has no basic oxide, but on the contrary has two acidic oxides forming salts (arsenites and arsenates) with metallic bases.

[*Bismuth*, although a very heavy metal of great lustre, forms few salts of definite composition, its basic functions being feeble.]

*Chromium*, while having the external properties of a metal, performs acidic functions in some salts (chromates and dichromates), but basic functions in other salts (as in chromium sulphate, chromium oxalate, and chrome alum).

*Manganese* is basic in manganous sulphate and other manganous salts, but it performs acidic functions in the manganates and permanganates.

*Molybdenum*, *tellurium*, *tungsten*, *uranium*, and *vanadium* have metallic physical properties, but do not perform the basic function in any oxygen salts; on the contrary they perform acidic functions forming molybdates, tellurates, tungstates, and vanadates. They are physically metals, but chemically non-metallic elements.

Arsenic, antimony and bismuth present obvious chemical relationships to nitrogen and phosphorus, which are in no sense metallic. Vanadium also belongs to the same group by virtue of its chemical analogies and atomic weight.

Tellurium closely resembles sulphur, *not* in any of its physical properties, but in the character and structure of its compounds.

*Tin* is a bright, heavy, malleable metal; but instead of such salts as sulphate, nitrate, or phosphate of tin, we have stannates of potassium and sodium. *Chemically* tin is, therefore, not a metal.

*Osmium* is one of the platinum group of "noble metals," has a brilliant metallic lustre, and is highly tenacious, ductile, and malleable; but instead of forming any basic oxide it forms "osmic acid," osmates, and osmites.

96. From the foregoing considerations it will be seen that a classification of the elements into metals and non-metallic elements according to their physical properties is not consistent with systematic chemistry in all cases; but it is nevertheless convenient and useful, for no method of classification of the elements has so far been proposed by which the difficulties referred to are wholly avoided or removed.

## CHAPTER V.

### THE LAW OF DEFINITE COMBINING PROPORTIONS AND THE ATOMIC THEORY.

**97.** It was pointed out by Proust that all chemical compounds contain their component elements in fixed and invariable proportions.

The following examples illustrate this:

a. Hydrogen and chlorine combine or unite with each other to form hydrochloric acid. The combining proportions of these two elements are in the hydrochloric acid, invariably as 1 part by weight of hydrogen to 35.4 parts of chlorine, or as any multiple of 1 to the same multiple of 35.4. The quantity of hydrochloric acid formed by 1 part of hydrogen and 35.4 parts of chlorine is 36.4 parts.

Hydrogen and chlorine can not be made to unite in any other proportions. If you should try to cause 1 gram of hydrogen to unite with 36.4 grams of chlorine, you would obtain exactly 36.4 grams of hydrochloric acid and 1 gram of free chlorine would be left over; and if you should use 2 grams of hydrogen for 35.4 grams of chlorine you would still get 36.4 grams of hydrochloric acid and 1 gram of hydrogen would be left over.

If 36.4 grams of hydrochloric acid be decomposed the products will be exactly 1 gram of hydrogen and 35.4 grams of chlorine.

b. Mercury and oxygen unite in two different proportions: in mercurous oxide we find, in round numbers, 200 parts of mercury united to 8 parts of oxygen, or 25 grams of mercury for every gram of oxygen; in mercuric oxide we find 200 parts of mercury united to twice 8 parts of oxygen, or 25 grams of mercury for every 2 grams of oxygen.

c. Nitrogen unites with oxygen in five different proportions. In round numbers these proportions are:

- 14 grams of nitrogen with 8 grams of oxygen.
- 14 grams of nitrogen with 16 grams of oxygen.
- 14 grams of nitrogen with 24 grams of oxygen.
- 14 grams of nitrogen with 32 grams of oxygen.
- 14 grams of nitrogen with 40 grams of oxygen.

Observe that the several proportions of oxygen that can unite with 14 grams of nitrogen are all simple multiples of 8 grams, and, in this case, the several combining quantities of oxygen stand to each other in the strikingly simple ratio of 1, 2, 3, 4 and 5.

d. It is found that in round numbers

1 gram of hydrogen unites with 16 grams of oxygen to form hydrogen dioxide.

2 grams of hydrogen unites with 16 grams of oxygen to form water.

14 grams of nitrogen unites with 3 grams of hydrogen to form ammonia.

14 grams of nitrogen unites with 16 grams of oxygen to form nitric oxide.

14 grams of nitrogen unites with  $3 \times 35.4$  grams of chlorine to form nitrogen chloride.

3 grams of hydrogen unites with  $3 \times 35.4$  grams of chlorine to form hydrochloric acid.

55 grams of manganese unites with  $3 \times 35.4$  grams of chlorine to form manganic chloride.

55 grams of manganese unites with 16 grams of oxygen to form manganous oxide.

$55 \times 2$  grams of manganese unites with  $16 \times 3$  grams of oxygen to form manganic oxide.

55 grams of manganese unites with  $16 \times 2$  grams of oxygen to form manganese dioxide.

4 grams of hydrogen unites with 12 grams of carbon to form "marsh-gas."

12 grams of carbon unites with 16 grams of oxygen to form carbon monoxide.

12 grams of carbon unites with  $2 \times 16$  grams of oxygen to form carbon dioxide.

16 grams of oxygen unites with 200 grams of mercury to form mercuric oxide.

200 grams of mercury unites with 35.4 grams of chlorine to form calomel.

200 grams of mercury unites with  $2 \times 35.4$  grams of chlorine to form mercuric chloride.

These comparisons might be extended to include every chemical compound known, with the same results—simple inter-rela-

tionships of the mass proportions between the different elements in all the compounds which they severally form with each other.

**98.** Two laws formulated by Dalton touching the definite combining proportions of the elements may be stated as follows:

**A. The Law of Definite Proportions.** Any given chemical compound always contains the same component elements in the same mass proportions.

**B. The Law of Multiple Proportions.** Whenever any two elements form more than one compound with each other, the different masses of one element combining with a fixed mass of the other element bear a simple ratio to each other.

**99.** The law of multiple proportions may also be stated thus: *Whenever any two elements unite with each other in more than one mass proportion it is invariably the case that simple multiples of a fixed mass unit of either of these elements unite with a fixed mass unit, or with simple multiples of a fixed mass unit, of the other.*

It may be illustrated as follows:

If the elements A and B form with each other two or more different compounds, then the different masses of A which combine with any given mass of B are simple multiples of a fixed relative mass.

The smallest relative combining mass unit of A may be [and, as a matter of fact, it probably always is] different from the smallest combining mass unit of B, but 1, or 2, or 3, or 4, or 5, or 6, or 7 of the mass units of A will be found to combine with 1, or 2, or 3, or 4, or 5, or 6, or 7 of the mass units of B, or the two will combine in the proportions of simple multiples of their respective combining mass units. If in any compound of A and B the combining mass of A be 17 and that of B 21, then, in any other existing or possible compound of the same elements, the combining mass of A is invariably a simple aliquot part or a simple multiple of 17, and the combining mass of B a simple aliquot part or a simple multiple of 21.

**100. The atomic theory.** John Dalton explained the definite combining proportions of the elements by the adoption of the very old hypothesis that all matter is composed of indivisible individual particles.

He assumed that these indivisible individual particles of each element, called *atoms*, have definite masses.

The atomic theory may be stated as follows: *Each element consists of indivisible atoms of fixed mass.*

All chemical compounds are produced by the union of these atoms.

**101. Atomic weight.** The mass of one atom of any element is the *atomic weight* of that element.

While all atoms of any given element have the same mass, the atomic weight of each element differs from that of any other element.

The *actual masses* or "absolute weights" of the atoms of the respective elements are unknown; but their *relative masses* or weights are assumed to be in most cases approximately accurately known.

The numbers expressing the atomic weights of the known elements are, therefore, the relative masses of the different kinds of atoms, and these numbers, as now generally given, refer to the mass of the hydrogen atom as the unit of expression. Thus the specific atomic mass of hydrogen is 1, and as the atom of oxygen, according to the latest determinations generally accepted, weighs 15.88 times as much as the atom of hydrogen, the specific atomic mass of oxygen is 15.88. The atomic weight of chlorine is 35.18 because one atom of chlorine weighs 35.18 times as much as one atom of hydrogen.

**The atomic weights are the smallest relative masses of elements entering into combination with other elements.**

**102.** But the atomic weights of the elements can be expressed in other than hydrogen units. Berzelius used the atomic mass of *oxygen* as the standard of comparison and expressed that mass by the number 100. Since the weight of the atom of oxygen is *about* 16 times as great as the weight of the hydrogen atom it follows that the relative masses of the atoms of oxygen and hydrogen are about as 16 to 1 if hydrogen be adopted as the standard and its atomic mass expressed by 1; they are as 100 to 6.25 if oxygen be taken as the standard of comparison and its atomic mass given the value of 100, for 16 is to 1 as 100 is to 6.25.

**103.** The atomic weights given in the first column of the table here presented are those published by Professor Frank W. Clarke in the Journal of the American Chemical Society in February, 1900. They are based upon Hydrogen=1, and the atomic

weight of Oxygen is taken to be 15.88, in accordance with the latest determinations.

The atomic weights given in the second column are deduced from those in the first column, but refer to Oxygen = 16, which makes the atomic weight of Hydrogen 1.008. The use of these values (based on Oxygen = 16) has gained ground among chemists because the atomic weights of the greater number of elements have been deduced either directly or indirectly from their oxygen compounds, the oxygen compounds are extremely numerous, nearly all elements combine with oxygen whereas not one-half of them combine directly with hydrogen, and the numbers derived from the standard Oxygen = 16 are more convenient on account of their less awkward fractions.

In the third column of the table I have placed the *approximately correct* atomic weights which will be found sufficiently accurate and most convenient for all ordinary purposes. These values are used throughout this book.

TABLE OF ATOMIC WEIGHTS.

NAME OF THE ELEMENT.	SYM- BOLS.	ATOMIC WEIGHTS.	
		According to F. W. Clarke.	Approximate.
		H=1. O=16.	
Aluminum .....	Al	26.9	27.
Antimony .....	Sb	119.5	120.
Argon .....	Ar	?	?
Arsenic .....	As	74.45	75.
Barium .....	Ba	136.4	137.
Beryllium .....	Be	9.0	9.1
Bismuth .....	Bi	206.5	208.
Boron .....	B	10.9	11.
Bromine .....	Br	79.34	80.
Cadmium .....	Cd	111.55	112.
Cæsium .....	Cs	131.9	132.9
Calcium .....	Ca	39.8	40.
Carbon .....	C	11.9	12.
Cerium .....	Ce	138.0	139.
Chlorine .....	Cl	35.18	35.4
Chromium .....	Cr	51.7	52.
Cobalt .....	Co	58.55	59.0
Columbium .....	Cb	93.0	93.7
Copper .....	Cu	63.1	63.6
Crypton .....	?	?	?
Erbium .....	Er	164.7	166.0
Fluorine .....	F	18.9	19.05
Gadolinium .....	Gd	155.8	157.0
Gallium .....	Ga	69.5	70.0
Germanium .....	Ge	71.9	72.5
Glucinum .....	Gl	9.0	9.1
Gold .....	Au	195.7	197.2

NAME OF THE ELEMENT.	SYM- BOLS.	ATOMIC WEIGHTS.	
		According to F. W. Clarke	Approximate.
Helium .....	He	?	?
Hydrogen .....	H	1.000	1.008
Indium .....	In	113.1	114.0
Iodine .....	I	125.89	126.85
Iridium .....	Ir	191.7	193.1
Iron .....	Fe	55.6	56.0
Lanthanum .....	La	137.6	138.6
Lead .....	Pb	205.36	206.92
Lithium .....	Li	6.97	7.03
Magnesium .....	Mg	24.1	24.3
Manganese .....	Mn	54.6	55.0
Mercury .....	Hg	198.5	200.0
Molybdenum .....	Mo	95.3	96.0
Neodymium .....	Nd	142.5	143.6
Neon .....	?	?	?
Nickel .....	Ni	58.25	58.7
Nitrogen .....	N	13.93	14.04
Osmium .....	Os	189.6	191.0
Oxygen .....	O	15.88	16.00
Palladium .....	Pd	106.2	107.0
Phosphorus .....	P	30.75	31.0
Platinum .....	Pt	193.4	194.9
Potassium .....	K	38.82	39.11
Praseodymium .....	Pr	139.4	140.5
Rhodium .....	Rh	102.2	103.0
Rubidium .....	Rb	84.75	85.4
Ruthenium .....	Ru	100.9	101.7
Samarium .....	Sm	149.2	150.3
Scandium .....	Sc	43.8	44.1
Selenium .....	Se	78.6	79.2
Silicon .....	Si	28.2	28.4
Silver .....	Ag	107.11	107.92
Sodium .....	Na	22.88	23.05
Strontium .....	Sr	86.95	87.6
Sulphur .....	S	31.83	32.07
Tantalum .....	Ta	181.5	182.8
Tellurium .....	Te	126.5	127.5
Terbium .....	Tb	158.8	160.0
Thallium .....	Tl	202.61	204.15
Thorium .....	Th	230.8	232.6
Thulium .....	Tu	169.4	170.7
Tin .....	Sn	118.1	119.0
Titanium .....	Ti	47.8	48.15
Tungsten .....	W	182.6	184.0
Uranium .....	U	237.8	239.6
Vanadium .....	V	51.0	51.4
Ytterbium .....	Yb	171.9	173.2
Yttrium .....	Yt	88.3	89.0
Zinc .....	Zn	64.9	65.4
Zirconium .....	Zr	89.7	90.4

104. The atomic weights which should be employed in the construction of working formulas for the preparation of pharmaceutical chemicals are the approximate atomic weights in the last column of the foregoing table. The differences between the

atomic and molecular weights given in this volume under the titles of elements and compounds and those of the pharmacopœias are so small that they may safely be ignored and the laborant may with entirely satisfactory and reliable results adopt any one of the three sets of atomic weights given in this table.

**105. Molecular weights.** As all molecules consist of atoms, and as all atoms have fixed masses, it follows that the weight of any molecule is the sum of the weights of the atoms contained in it.

All molecules of the same kind have the same mass, because all molecules of any one kind of matter contain the same kind or kinds of atoms, the same total number of atoms, and the same number of each kind of atoms.

Each distinct kind of matter, whether elemental or compound, accordingly has a fixed molecular mass or weight.

The molecule of hydrogen contains two hydrogen atoms; therefore, if the atomic weight of hydrogen be 1, its molecular weight must be 2.

The molecule of oxygen is also diatomic, and as its atomic weight is 16 its molecular weight is 32.

The molecule of water contains three atoms, of which two are hydrogen atoms and the third an oxygen atom. Hence the molecular weight of water must be 18.

**106.** The atomic hypothesis is supported by the following facts:

a. The fixed combining proportions of the elements have been determined by analyses and syntheses of numerous compounds.

b. *All atoms have the same capacity for heat* (Law of Dulong and Petit) as demonstrated by the established fact that it requires exactly the same amount of heat to raise the temperature of any atom of any kind one degree, the "specific heat" of each element being inversely as its atomic weight.\*

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\* By *Specific Heat* is meant the relative quantity of thermal energy (or heat) necessary to raise the temperature of a given mass of any substance one thermal degree.

Specific heat is expressed in units of the specific heat of water, which is taken as the standard of comparison. Thus the quantity of heat required to raise the temperature of one weight unit of water one degree, or the specific heat of water is = 1. But only  $\frac{8190}{100,000}$  as much heat or thermal energy is required to raise the temperature of the same mass or weight unit of mercury one degree, and the specific heat of mercury is, therefore, 0.0319.

c. The numbers expressing the respective "vapor densities"\* of all substances are one-half of the magnitude of the numbers expressing their molecular weights, and it, therefore, follows that the atomic weights of all elements having diatomic molecules coincide with their vapor densities, which accordingly serve to verify atomic weights.

d. The natural classification of the elements into groups ac-

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The atomic weight of any element may be deduced from or verified by its specific heat, for, inasmuch as all atoms of whatever kind have the same capacity for heat, it follows that the product obtained by multiplying the atomic weight by the specific heat of the same element is a constant number. That number is found to be approximately 6.40. Hence when 6.40 is divided by the specific heat the quotient must be, approximately, the atomic weight.

The number obtained by multiplying the specific heat of an element by its atomic weight is called its *atomic heat* (approximately 6.4).

Thus the atomic heat of any element divided by its specific heat gives its atomic weight; the atomic heat divided by the atomic weight gives the specific heat; and the specific heat multiplied by the atomic weight gives the atomic heat.

Neumann and Regnault proved that the specific heats of *compounds* are inversely proportional to their *molecular* weights, just as the specific heats of *elements* are inversely as their *atomic* weights.

After further investigations by Regnault and others the conclusion was accepted that all atoms, free or combined, have the same capacity for heat.

The sum of the atomic heats of the atoms of any molecule is the molecular heat of that molecule. Therefore, the molecular heat of any compound divided by the number of atoms contained in its molecule must give a quotient which is the mean of the atomic heats of its component elements (or, in other words, a quotient of approximately 6.4.) Hence if the molecular heat of any substance is divided by 6.4, the quotient expresses the number of atoms contained in the molecule.

Atomic and molecular weights may therefore be deduced from or verified by the specific heats of substances.

All elements whose atomic weights exceed 30 obey the law of Dulong and Petit at common temperatures. Other elements, as S, P, F, O, Si, B, H, C and Be, have atomic heats which are smaller than those closely corresponding to that law. But at sufficiently high temperatures it seems probable that all elements obey the law, for H. F. Weber found that carbon, silicon and boron obey the law at temperatures exceeding 100°, and Nilson, Petterson and Humpidge showed that beryllium also follows the rule.

\* The specific ~~heat~~ of any kind of matter in the gaseous state is called its vapor density. It is always expressed in units of the density of hydrogen. Hence the vapor densities of all elemental molecules containing the same number of atoms stand to each other in exactly the ratio of their respective atomic weights. Thus the vapor density and the atomic weight of hydrogen being 1, the vapor density and atomic weight of oxygen is 16; etc.

But the vapor densities of different kinds of matter at certain temperatures are, in several instances, known to become reduced to one-half at higher temperatures, and it is assumed that in these cases the molecules are split in two by the heat motion. Examples of this division of molecules are furnished by iodine, two of the oxides of nitrogen and ferric chloride.

*weight*

cording to their chemical properties (such as their polarity and valence) and according to the structure and properties of the compounds they form, confirms the atomic theory, for such a classification actually results from the arrangement of the elements, in the order of their atomic weights, in periods (as will be shown in the chapter on the Periodic System).

e. Many other facts which have been experimentally determined, independently of each other, directly or indirectly confirm the atomic hypothesis, and all facts of chemistry at present known agree with it.

107. If it be assumed that the atomic theory is true, then the fixed combining proportions by weight are thereby explained and seen to be the inevitable result of the fixed atomic masses. If, on the other hand, the atomic theory be rejected, then the fixed combining weights of the elements remain unintelligible, for no other sufficient explanation thereof has yet been made.

The atomic hypothesis is a lucid and reliable working hypothesis, and the system of chemistry built upon it leads to fixed results which may be predicted and obtained with absolute certainty and uniformity.

108. As the density of hydrogen is the unit chosen for the expression of the relative densities of all other gases, it follows that if the weight of any given volume of any gas be divided by the weight of the same volume of hydrogen the quotient is the number expressing its density.

109. It is an accepted hypothesis that **equal volumes of all gases contain the same number of molecules** (Avogadro's Law).

The atomic weight of hydrogen being the unit of expression of all atomic weights it follows that the molecular weight of hydrogen is 2, for each molecule of hydrogen contains two atoms.

The density of hydrogen being 1 and its molecular weight 2, it follows that the molecular weight of any substance is expressed by the number obtained when its vapor density is multiplied by 2.

110. The atomic weights of all elements having diatomic molecules (2 atoms in each molecule) coincide with their respective vapor densities.

The atomic weight of hydrogen is 1 and its vapor density is also 1.

The atomic weight of oxygen is 16 and one cubic-decimeter of it weighs 16 times as much as one cubic-decimeter of hydrogen weighs.

The atomic weight of nitrogen is 14, and the weight of 1 liter of nitrogen is 14 times the weight of 1 liter of hydrogen.

111. If the molecule of a given element contain but one atom, then the atomic weight of that element coincides with its molecular weight and is equal to twice the number expressing its vapor density.

As the vapor density of mercury is 100 (one cubic-decimeter of its gas weighing 100 times as much as the weight of one cubic-decimeter of hydrogen), its atomic weight is 200 and that is also its molecular weight. Hence its molecule must be monatomic.

112. The atomic weight of an element having tetratomic molecules (molecules containing 4 atoms) must be equal to one-half of its vapor density.

113. From what has been stated in the preceding paragraphs it follows that **gaseous elements combine in simple volume proportions**, and that the volumes of the products bear simple relations to the volumes of the factors (Gay-Lussac).

To make this fact plain to the student we will assume that one volume of hydrogen contains 10 molecules of that element. According to the hypothesis of Avogadro one (equal) volume of chlorine must contain the same number. It has been shown that one molecule of hydrogen contains at least two atoms and there are sufficient reasons for the assumption that it does not contain more than two atoms. For good reasons it is assumed that the molecules of chlorine are also diatomic. Therefore one volume of hydrogen would contain 20 atoms, and one volume of chlorine 20 atoms. When mixed and caused to unite chemically one volume of hydrogen and one volume of chlorine will form exactly two volumes of gaseous hydrochloric acid, made up of the 40 atoms of the two elements, and as each volume of gaseous hydrochloric acid must contain the same number of molecules of hydrogen chloride as one volume of hydrogen contains of hydrogen, two volumes of hydrochloric acid contain 20 molecules and each molecule must accordingly contain two atoms—one of hydrogen and one of chlorine.

For the same reasons 2 liters of hydrogen and 1 liter of oxygen will produce 2 liters of water vapor (the molecules of water being triatomic); and 3 liters of hydrogen with 1 liter of nitrogen will produce 2 liters of gaseous ammonia (the molecule of ammonia being tetratomic).

## CHAPTER VI.

### CHEMICAL POLARITY.

**114.** Reference has already been incidentally made to the *law of opposites* in chemistry and to positive and negative polarity (Chapter IV).

All chemists recognize this law of opposites, directly or indirectly. Its existence is clearly demonstrated by its decided bearing upon atomic valence (see "polarity value," Chapter IX), by the unerring precision with which reactions involving oxidation and reduction are explained in the light of polarity, and by its manifestly important relation to the natural classification of the elements (the "Periodic System").

The law of chemical opposites is most strikingly indicated by the opposite properties and behavior of acids and bases which have been briefly described. It was stated that acids do not combine with or neutralize other acids, and that bases do not combine with or neutralize other bases, but that acids neutralize bases and bases neutralize acids, because acids and bases are chemical opposites, and they are opposites because of the opposite character of basic and acidic functions.

A repetition of some of the facts already presented will aid many students and is, therefore, made as follows:

The most characteristic and powerful acids are corrosive, sour or "acid," and turn blue litmus red.

The most characteristic and powerful bases (the alkalies) are caustic, alkaline or lye-like, and turn red litmus blue.

When a red solution of litmus is turned decidedly blue by an alkali, it can be rendered red again by the addition of an acid; and when a blue solution of litmus has been changed to red by an acid it may be rendered blue again by the addition of an alkali.

When certain fixed proportions of a strong acid and a strong alkali are mixed, they mutually neutralize each other's properties so that the resulting compound is not corrosive or caustic, neither acid nor alkaline, and does not change the color of either blue or red litmus solution or litmus paper.

**115.** The existence of the law of opposites thus plainly indicated finds expression in various technical terms employed in the discussion of chemical theories and phenomena, and the systems of chemical notation and nomenclature in use rest upon the recognition of the fact that chemical attraction and combination depend upon the relatively opposite character of the atoms directly united.

This attraction between opposites, combination of opposites, and mutual saturation or neutralization of opposites in chemistry must be intelligently expressed. The opposite qualities of the chemical affinities by which any two atoms unite with each other are, therefore, likened to the opposite polarities recognized in electricity. The term "chemical polarity" is as well warranted in chemistry as the term electrical polarity is in electrical terminology, and the terms "positive" and "negative" as applied to the respective combining qualities of the atoms and radicals which unite with or neutralize each other in chemical action are as appropriate as the same terms when used in connection with the opposite polarities concerned in electrical action.

This use of the same technical term to express analogous ideas and phenomena in chemistry and electricity should not and does not prevent proper distinction between these different kinds or modes of manifestation of energy.

**116.** The quality of the chemism of any atom is indicated by the general character, structure and properties of the compounds it forms.

**All atoms exhibit, in their chemical compounds, one or the other, or both, of two opposite qualities termed positive polarity and negative polarity, respectively.**

An atom is, therefore, according to its *chemical polarity*, either 1, a **Positive Radical**; or 2, a **Negative Radical**; or 3, it is partly positive and partly negative (when united by a part of its valence units to a positive element and by the remainder of its valence to a negative element).

**117.** Radicals capable of uniting with each other to form molecules must be of opposite chemical polarities, and any two atoms uniting directly with each other are thus united by reason of the attraction which attends that opposite polarity of their combining affinities.

**Positive radicals can not unite with other exclusively positive**

radicals, nor can negative radicals unite with other exclusively negative radicals.

But positive radicals unite with negative radicals and *vice versa*.

One positive radical can take the place of another positive radical, and a negative radical can be replaced by another negative radical, without any change in the general structure of the molecule.

**118. Hydrogen exhibits positive chemical polarity with respect to all other elements.**

**119. Oxygen exhibits negative chemical polarity with respect to all other elements.**

**120.** The chemical polarity of any atom other than hydrogen or oxygen may be determined by its analogy to one or the other of these elements as to its position, exchangeability, and functions, in the molecule in which it is contained, and by the general character and properties of its compounds.

**121.** Any radical taking the place of the hydrogen contained in any compound molecule, forming a new molecule of similar structure and general chemical character, is, like hydrogen itself, a positive radical.

**122.** Any radical taking the place of the oxygen contained in any compound molecule, forming a new molecule of similar structure and general chemical character, is, like oxygen itself, a negative radical.

**123.** Any radical which, by all or a part of its combining power, is directly united to hydrogen is, to that extent, and under such conditions, a negative radical.

**124.** Any radical which, by all or a part of its combining power, is directly united to oxygen is, to that extent, and under such conditions, a positive radical.

**125.** The metallic elements which do not unite directly with hydrogen by interatomic linking are positive radicals in all of their compounds.

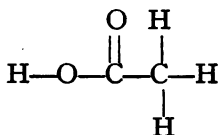
**126.** Elements having some of the physical properties of metals but forming chemical compounds with hydrogen by the direct union of the atoms of both elements, are, like most of the non-metallic elements, capable of exercising negative polarity in some compounds and positive polarity in others.

**127.** Chemical polarity is only a relative function, and any

element capable of combining directly with either hydrogen or oxygen must be negative whenever it is united to hydrogen, but positive whenever it is united to oxygen.

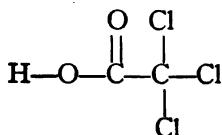
Thus chlorine in direct combination with hydrogen is negative chlorine, but chlorine in direct combination with oxygen is positive chlorine.

Let the carbon atom be represented by C, the hydrogen atom by H, and the oxygen atom by O. Then the molecule of acetic acid, which contains those three elements may be represented by the formula



This formula shows that the two carbon atoms are united or linked to each other while at the same time one of them is also united to oxygen and the other to hydrogen; hence both carbon atoms must be partly positive and partly negative, unless the first is exclusively positive and the second exclusively negative.

The compound called trichloroacetic acid is analogous to acetic acid and may be represented by the formula

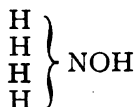


In this formula we have chlorine, represented by Cl, in place of the three hydrogen atoms which we found united to the second carbon atom in the molecule of acetic acid. The element chlorine is generally referred to as a characteristic negative element; yet it has here apparently replaced the invariably positive element, hydrogen. But chlorine as well as carbon may be either positive or negative, or partly positive and partly negative, as will be more fully shown later.

**128.** Whenever any atom is directly combined with both hydrogen and oxygen *at the same time*, its chemical polarity must be partly negative and partly positive.

The chemical compound known as ammonium hydroxide is

composed of four hydrogen atoms united directly to one nitrogen atom (N), while the same nitrogen atom is also directly united to one oxygen atom attached to a fifth hydrogen atom, thus:



The nitrogen atom in this molecule is negative toward the hydrogen, but positive toward the oxygen.

Any atom capable of combining immediately and at one time with two or more other elements may or may not then exhibit divided or double polarity.

In ammonium chloride there is but one nitrogen atom, and that is united to positive hydrogen on one hand and to negative chlorine on the other ( $\text{H}_4\text{NCl}$ ).

When one carbon atom unites with both chlorine and hydrogen that carbon is negative in its relation to the hydrogen and positive in its relation to the chlorine ( $\text{H}_3\text{CCl}$ ,  $\text{H}_2\text{CCl}_2$ ,  $\text{HCCl}_3$ , etc.).

**129.** The chemical polarity of an uncombined atom is only *potential* and undetermined; but the polarity of any radical in combination is *actual* and determined by the atom to which it is directly united.

The potential chemical polarity of an uncombined compound radical containing oxygen is always negative if the combining power of that oxygen is only partially occupied. The polarity of any compound radical is the polarity assumed by that atom by means of which it may be united to another radical.

The chemical polarity of the compound radical hydroxyl (HO) is negative because it is composed of one hydrogen atom and one oxygen atom, and the combining power of the positive hydrogen is fully satisfied or saturated, while the combining power of the negative oxygen is only one-half saturated. This radical, then, combines with other radicals by means of the combining power remaining in its oxygen.

**130.** The term "chemical polarity" and the terms "positive" and "negative" polarity had their origin in the observed analogies between electrical and chemical attraction, whence arose the "electro-chemical theory" of Berzelius. But the theory of chemical polarity as now understood is essentially different from that held

by Berzelius and is in harmony with accepted modern chemical philosophy.

131. Electrical energy may be produced by chemical action, and chemical decomposition may be effected by means of electricity.

Certain classes of chemical compounds, called *electrolytes*, which include acids and salts, can be decomposed in that manner. This chemical decomposition by electrical energy is called *electrolysis*.

If the electric current be caused to pass through a solution of the electrolyte, decomposition of the electrolyte follows; the positive radical of the electrolyte—as the hydrogen of an acid, the metal of a metallic salt, etc.—is always liberated at the negative electrode, and the negative radical of the electrolyte—as oxygen, chlorine, bromine, iodine, hydroxyl, and any one of the compound acid-radicals—is always liberated at the positive electrode.

The products of electrolysis are called *ions*, and, as the positive electrode is called the *anode* and the negative electrode the *cathode*, the negative ions are called *an-ions* and the positive ions are called *cath-ions*.

According to Arrhenius and Planck the water-solutions of acids, bases and salts contain these compounds to a greater or less extent separated into their respective ions. Hence an aqueous solution of potassium chloride must contain both of its constituent elements in the free state. Ostwald says in support of this conclusion that “the chlorine and the potassium in solutions of potassium chloride are the elements *in the atomic condition* \* \* \* and charged with enormous quantities of positive and negative electricity, respectively,” while potassium as a metal which decomposes water so violently, and chlorine as a greenish strong-smelling gas, are *molecular combinations*. Ostwald further says that “the phenomena of electrolysis force us to the conclusion that parts of the molecules, or ions, of acids, bases and salts are contained, like free molecules, in their solutions” and that the extent of the dissociation of the molecules into their respective ions is in proportion to their dilution, so that the dissociation of the whole of the dissolved salt occurs, theoretically speaking, only in infinitely dilute solutions.

Again, Ostwald says: “There is no reagent for detecting sodium chloride; the reagents used detect only chlorine and sodium; and these reagents are effective for all solutions in which chlorine, on the one hand, and sodium, on the other hand, are present as ions. A substance which is not present as an ion ceases to show the characteristic reactions of that substance. Silver is a reagent for chlorine, but silver does not show the presence of chlorine in the perchlorates. This is because the ions of these

salts are, e. g., K and  $\text{ClO}_4$ ; chlorine is not an ion of the perchlorates, and these salts, therefore, do not show the reactions for chlorine. But if a perchlorate is changed to a chloride by heat, a solution of the chloride shows the chlorine-reaction because chlorine-ions are now present."

With regard to the colors of salt solutions Ostwald says: "The colors of salt solutions are essentially the colors of the parts of molecules, or ions, contained therein, and all salt solutions which contain a certain ion must exhibit the characteristic color of that ion. Should the expected color not appear, we may conclude that the corresponding ion is absent."

"The red color of dilute solutions of cobalt salts, for instance, indicates the presence of cobalt-ions. The sulphate, nitrate, chloride, etc., have the same color in solution; *the color is independent of the negative ions*. If one of these solutions is boiled with an excess of potassium cyanide, it is decolorized, and *the colorless solution no longer shows the reactions of cobalt*. The compound potassium cobalticyanide,  $\text{K}_3\text{Co}(\text{CN})_6$ , has been formed; the ions of this compound are  $3\text{K}$  and  $\text{Co}(\text{CN})_6^-$ ; free cobalt-ions are no longer present."\*

**132.** The metal is the basic positive radical in any metallic salt.

The basic metal can not be replaced by any non-metallic element except hydrogen. It can be replaced by hydrogen.

Hydrogen is invariably a positive radical. And when the metal of a metallic salt is replaced by hydrogen, the compound is transformed into an acid, for acids are the salts of hydrogen.

Sulphate of copper is a metallic salt, being the salt formed by copper with sulphuric acid, which is the sulphate of hydrogen. In other words, the only difference between these two compounds is that one contains copper and the other hydrogen united to the negative radical called the sulphate radical, which is the same in all sulphates.

**133.** When acids and bases neutralize each other and thus form salts, the acids contribute the compound negative acid-radicals and the bases contribute the basic positive radicals toward the formation of those salts.

**134.** A classification of salts according to their positive radicals is systematic, and brings out in each class certain general properties derived from said positive radicals. Such a classification would place the salts of potassium in one class, the salts of iron in another, the salts of copper in a third class, and so on.

A classification of salts according to their negative radicals is

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\* SOLUTIONS, by W. Ostwald, translated by M. M. Pattison Muir, London; Longmans, Green & Co., 1891.

also systematic, but it brings out a different set of general properties of each class, derived from the negative radicals. Such a classification would place the nitrates in one group, the sulphates in another, the carbonates in still another, etc.

**135.** The basic positive radical of a salt may be replaced by another and equivalent positive radical without altering the general structure of the salt; and the negative or acidic radical may be replaced by another and equivalent similar radical without any change in the general structure of the compound. But the basic radicals of salts can not in any such way be replaced by acidic radicals, nor the acidic radicals by basic ones.

**136.** Assuming that the molecule of hydrogen contains two hydrogen atoms we must of necessity conclude that one of these hydrogen atoms must exercise positive polarity and the other must be of negative polarity in order that they may be capable of uniting with each other. The recognition of the existence of that condition which is called chemical polarity, and of the assumption that chemical attraction results from opposite polarities, carries with it the doctrine that in all elemental molecules consisting of two atoms the polarity of each of these atoms must be opposite to that of the other, unless, indeed, each atom exercises both positive and negative polarity at the same time.

To illustrate this let O represent one atom of oxygen and let the signs + and — indicate positive and negative polarity, respectively. Then one molecule of oxygen, composed of two oxygen atoms, may be represented either by  $O+—O$  or by  $O\begin{smallmatrix} + \\ - \end{smallmatrix} O$ .

**137.** The fact that chemical polarity is but a relative property or condition may be further illustrated by many other examples.

Sulphur is negative in all sulphides but positive in all sulphates and sulphites.

Nitrogen is negative in ammonia but positive in all nitrates and nitrites.

Carbon is negative in methane and in the carbides of the metals, but positive in carbon disulphide and in the carbonates.

Chlorine is positive in all chlorates but negative in all chlorides.

**138.** Oxygen and fluorine are the only two elements which exercise invariably or exclusively negative polarity in all their

compounds. These two elements do not combine with each other.

**139.** Twelve elements are sometimes negative and sometimes positive, namely: carbon and silicon; nitrogen, phosphorus, arsenic and antimony; sulphur, selenium and tellurium; and chlorine, bromine and iodine.

Of these elements antimony is the only one said to exercise basic functions, and that only feebly and rarely .

## CHAPTER VII.

### THE RELATIVE INTENSITY OF THE CHEMICAL ENERGY OF THE DIFFERENT ELEMENTS.

140. The respective elements differ widely as to the relative intensity of their chemism.

It has already been stated that monatomic molecules are rare because free atoms are generally irresistibly impelled by their chemism to unite with other atoms of their own kind or of other kinds to form molecules in which all the combining power of each component atom is satisfied or used.

But many atoms contained in elemental molecules consisting of more than one atom display great chemical energy while others appear to be relatively indifferent. Finally, the elements betray striking differences in this particular even when in combination with other elements.

141. That elements in their atomic state are far more energetic in their chemical action than they are in their molecular condition is illustrated by the following examples:

Molecules of sulphur and molecules of hydrogen do not affect each other; the sulphur may be placed in a bottle together with hydrogen and the two elements allowed to remain in contact with each other a long time without any indication of chemical affinity between them. But atomic sulphur and atomic hydrogen in their *nascent state*, or at the instant of their separation from other molecules, do unite (as when iron sulphide and sulphuric acid react upon each other).

If the gaseous element hydrogen be passed through a tube into a bottle containing dilute nitric acid the hydrogen will have no effect whatever upon the acid, no matter how copious the quantity of the gas nor how long continued its current. But if hydrogen be generated or liberated in the nitric acid itself (by dissolving metallic zinc in cold dilute nitric acid), then the "nascent hydrogen," or atomic hydrogen, or the hydrogen atoms before they unite with each other to form molecules of hydrogen, attack and decompose another portion of the nitric acid forming am-

monia and water ( $\text{HNO}_3 + 8\text{H} = \text{H}_3\text{N} + 3\text{H}_2\text{O}$ ), so that the resulting solution will contain not only zinc nitrate but also ammonium nitrate.

Triatomic molecules of oxygen, called "ozone," show great chemical energy because each such molecule readily gives up one of the oxygen atoms, being thus changed into a diatomic molecule of greater stability, while the liberated atom in its *status nascendi* vigorously attacks molecules of other substances.

142. The relative intensity of the chemical energy of elements in their molecular condition is exemplified by the following:

Fluorine uncombined with any other element can be studied only with the greatest difficulty, if at all, because it attacks nearly all other substances with such energy that molecules of fluorine are not formed, but the fluorine atoms enter into combination with other kinds of atoms. Fluorine decomposes glass, sodium chloride, and water. It takes the hydrogen away from water.

Chlorine and bromine are also very energetic in their chemical action, but not as powerful as fluorine. In their action upon water both chlorine and bromine resemble fluorine in that they combine with the hydrogen of the water, setting the oxygen free.

Potassium and sodium, to prevent their oxidation, must be preserved immersed in liquid hydrocarbons. They immediately oxidize when exposed to the air. When put in water they at once decompose it, taking from it its oxygen and liberating its hydrogen.

Fluorine, chlorine and bromine, therefore, show a greater affinity for hydrogen than for oxygen, while potassium and sodium have an intense affinity for oxygen but never combine chemically, or by direct atomic linking, with hydrogen.

Crystallized silicon, adamantine boron, metallic antimony, and sulphur do not display any chemical energy when brought in contact with any one of nearly all other substances; but they immediately ignite in fluorine gas, and fluorine combines directly with all other elements except oxygen, nitrogen and carbon. Fluorine is the only known element which does not combine with oxygen.

Phosphorus, when brought in contact with oxygen, ignites and burns fiercely. It decomposes potassium chlorate with great violence.

As examples of elements having little or no chemical energy we may mention argon, nitrogen, gold and platinum.

Argon is a newly discovered gaseous constituent of the air; it exhibits no disposition to combine with other elements.

Extraordinary means are necessary to compel nitrogen atoms to combine with atoms of other kinds, and a great majority of the elements, including all the metals, form no chemical compounds in which they unite directly with hydrogen. Most of the compounds formed by nitrogen show a remarkable tendency to decompose, often with explosive violence.

**143.** The relative intensity of the chemical energy of the different compound acid-radicals (which are the compound radicals forming acids by combining with hydrogen) is indicated by the relative energy of the acids formed by them respectively.

When the inorganic hydroxyl acids are compared as to their action upon metals and metallic salts and upon various other kinds of matter, it is found that some of these acids are more energetic, or are "stronger" or more corrosive or destructive than others. Thus sulphuric acid decomposes the salts of boric acid, and sulphuric acid is fearfully destructive to organic tissues, while boric acid shows no tendency to decompose organic matter.

As all inorganic hydroxyl acids consist of but three elements, two of which (hydrogen and oxygen) are common to all of them, the differences between them as to their relative chemical energy must depend upon the third element, which is the acid-forming, positive element.

**144.** Bases as well as acids differ in regard to their chemical energy.

Potassium hydroxide ("caustic potash") is the "strongest" of the common bases. Magnesium hydroxide, lead hydroxide, and other bases are "weaker." All basic hydroxides contain hydrogen and oxygen in the form of hydroxyl (HO), and hence the differences between the several metallic bases in all respects must depend upon the metallic element to which the hydroxyl is united.

Potassium is a more powerful positive base-forming element than magnesium, and magnesium is a stronger basic element than lead.

**145.** The relative intensity of chemical energy exhibited by different elements must be directly and intimately connected with

or dependent upon their polarity, valence, and atomic weight, for the intensity of the combining energy of the most powerful positive base-forming elements is in direct ratio as their atomic weights, while the intensity of the chemical combining energy of the most powerful elements of negative polarity is in inverse ratio as their atomic weights. Thus the most powerful alkali metal is that having the largest atomic weight, and the weakest alkali metal is that possessing the smallest atomic weight; but the most energetic of the negative elements (the halogens) which combine, atom for atom, with the alkali metals is that which has the smallest atomic weight, and the weakest of the same family of elements of negative polarity is that of the largest atomic weight. At the same time it is found that elements exercising a relatively low atomic combining value (or valence) are, as a rule (not without apparent exceptions), more energetic and powerful chemical factors than those exercising a relatively higher atomic combining value (or valence).

To illustrate these facts we will present here a table of two families of positive elements and two families of negative elements, with their atomic weights:

#### POSITIVE ELEMENTS.

Lithium .....	7	Beryllium .....	9
Sodium .....	23	Magnesium .....	24
Potassium .....	39	Calcium .....	40
Rubidium .....	85.5	Strontium .....	87.5
Cæsium.....	133	Barium .....	137.5

#### NEGATIVE ELEMENTS.

Oxygen .....	16	Fluorine .....	19
Sulphur .....	32	Chlorine .....	35.4
Selenium .....	79	Bromine .....	80
Tellurium .....	127.5	Iodine .....	126.5

Of the elements named in this table any one of all that are placed in the first column of the positive elements combines, atom for atom, with any one of all that are placed in the last column of the negative elements; and any one of all that are put in the second column of the positive elements combines with any one of all that are put in the first column of the negative elements, atom for atom. But two atoms are necessary of any element in the first column of the positive elements to form a chemical compound with any one of the elements in the first column of the negative elements, and two atoms of any one of the elements in the second column of the negative elements are necessary to form

a chemical compound with any one of the elements in the second column of the positive elements.

The numbers represent the atomic weights.

The most strongly positive element in the first column is *cæsium*, next is *rubidium*, then *potassium*, *sodium* and *lithium* in the order named. In the second column the most powerful basic element is again the one at the foot, having the greatest atomic weight, and the chemical energy of the other elements of the same family, or in the same column, decreases as the atomic weight diminishes.

But of the negative elements the most energetic of all is *fluorine*, and in the same column (which includes all of the elements called *halogens*), *chlorine* is more energetic as a negative radical than *bromine*, and *iodine* is the least energetic. In the second column *tellurium* is the least energetic and *oxygen* the most powerful radical.

The alkali metals—those in the first column—are more strongly basic than those of the second column; and the *halogens* are more powerful negative elements than those in the *sulphur* family.

**146.** In illustration of the differences between several metals as basic positive radicals we may refer to the fact that the hydrogen of *nitric acid* (which is *hydrogen nitrate*) is replaced by the metals *silver*, *copper*, *lead*, *zinc*, *calcium* and *sodium*, in the order in which they are enumerated.

All *nitrates* contain the elements *nitrogen* (N) and *oxygen* (O), and each *nitrogen* atom is directly united to three *oxygen* atoms in every *nitrate*; hence the characteristic compound radical of all *nitrates* is represented by  $\text{NO}_3$ . The *nitrates* of *hydrogen*, *silver*, *copper*, *lead*, *zinc*, *calcium* and *sodium* are respectively represented by the following formulas:

$\text{HNO}_3$  is *hydrogen nitrate*;

$\text{AgNO}_3$  is *silver nitrate*;

$\text{Cu}(\text{NO}_3)_2$  is *copper nitrate*;

$\text{Pb}(\text{NO}_3)_2$  is *lead nitrate*;

$\text{Zn}(\text{NO}_3)_2$  is *zinc nitrate*;

$\text{Ca}(\text{NO}_3)_2$  is *calcium nitrate*;

$\text{NaNO}_3$  is *sodium nitrate*.

All of these *nitrates* are *water-soluble salts*.

*Silver* dissolves in *nitric acid*, forming *silver nitrate* by replac-

ing the hydrogen of the acid; copper added to the solution of the silver nitrate causes the silver to be separated by usurping its place and thus forming copper nitrate; lead put into the solution of the copper nitrate displaces the copper, throwing it out of the solution, and forms lead nitrate; the zinc, in turn, when added to the solution of the lead nitrate, dispossesses the lead of the nitrate radical, forming zinc nitrate; when calcium hydroxide  $[\text{Ca}(\text{OH})_2]$  is added to the solution of zinc nitrate the metals calcium and zinc exchange places and calcium nitrate results  $[\text{Zn}(\text{NO}_3)_2 + \text{Ca}(\text{OH})_2 = \text{Ca}(\text{NO}_3)_2 + \text{Zn}(\text{OH})_2]$ ; and when sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) is added to the solution of calcium nitrate the products formed are calcium carbonate and sodium nitrate  $[\text{Ca}(\text{NO}_3)_2 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + 2\text{NaNO}_3]$ .

In these successive *substitutions* of one metal for another it would appear that zinc is a stronger basic positive radical than lead; that lead is a more powerful positive element than copper; that copper is more strongly positive than silver; and that silver, in turn, is a more decidedly basic element than hydrogen and has a stronger affinity for the nitrate radical than the hydrogen has.

The several positive elements named may, however, stand in a different order as to their relative affinities *for some other negative radical and under different conditions*.

**147.** An arrangement of the elements and the compound radicals in the order of their relative energy or power, and according to their chemical polarity, is extremely difficult if not impossible.

A table of the elements arranged according to the assumed relative intensity of their ruling chemical polarity was prepared by the great chemist Berzelius, and was called the "electro-chemical series." That table was amended by various chemists from time to time as required by the results of new investigations, but it is rarely referred to at the present time because of the apparently insurmountable difficulties encountered in the effort to reconcile the conclusions reached in that direction with other at least equally probable deductions from chemical facts and analogies.

One of the difficulties is that certain elements assume positive polarity in some of their compounds and negative polarity in others. Thus negative chlorine is a very powerful radical forming relatively stable compounds, whereas positive chlorine forms relatively unstable molecules. Positive nitrogen forms much less

stable compounds than negative nitrogen, and negative sulphur generally forms molecules of greater stability than is possessed by the molecules formed by positive sulphur.

Another difficulty presents itself in the fact that certain metals are capable of performing acidic functions in some of their compounds and basic functions in others, and that they do not exhibit the same degree of chemical power in one rôle as in the other.

Finally the "selective affinity" of elements and the relative stability of their compounds depend to a great extent upon physical conditions, as will be shown in the chapter devoted to the influences affecting chemical changes.

**148.** Very energetic radicals generally form comparatively stable compounds with other powerful radicals of opposite polarity, while the compounds formed by radicals of relatively indifferent combining energy are less stable.

Moreover, the characteristic properties of powerful acidic radicals are not fully neutralized except by equally powerful basic radicals.

When a weak base forms a salt with a strong acid, the salt, if water-soluble, exhibits an acid reaction, or turns blue litmus red.

When, on the other hand, a weak acid forms a salt with a strong base, the salt, if water-soluble, exhibits an alkaline reaction, or turns red litmus blue.

But a salt formed by a powerful base with a powerful acid is neutral to litmus.

**149. Selective affinity.** If a potassium atom be so placed as to have the power to combine with either a chlorine atom, a bromine atom, or an iodine atom, it will in every such instance combine with the chlorine atom and not with either of the other two; and the potassium atom has greater affinity for an atom of bromine than for an atom of iodine. The chlorine atom has greater affinity for an atom of cæsium than for any other atom, and a greater affinity for barium than for calcium.

This preference is called *selective affinity* and it depends upon the relative intensity of the combining energy of the respective elements of opposite polarity. Potassium being a positive element has greater affinity for chlorine than for iodine because chlorine is a more powerful and energetic negative element than iodine.

## CHAPTER VIII.

### ATOMIC VALENCE.

**150.** No one individual atom of any kind can combine directly with more than six atoms of any one other kind.

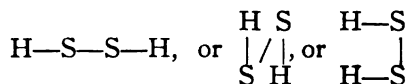
The hexachloride of tungsten is composed of one atom of tungsten directly united to six chlorine atoms; it is an example of the "highest chloride" possible to any element.

**151.** No one individual atom of any other element can hold in direct combination with itself more than four hydrogen atoms, nor more than four oxygen atoms.

**152.** No one individual atom of any other element can form more than one binary hydrogen compound, because **the number of hydrogen atoms which can be held in direct combination by a single atom of any given other element (to form a saturated binary molecule) is a constant number.**

Thus one atom of chlorine unites with one atom of hydrogen, forming a compound called hydrochloric acid, which is hydrogen chloride. The atoms of chlorine and hydrogen can not unite directly in any other numerical proportions.

One atom of sulphur unites with two atoms of hydrogen, forming hydrogen sulphide, and no other compound of sulphur and hydrogen *containing only one sulphur atom* is possible in which all of the sulphur is directly united to all of the hydrogen. A compound called hydrogen disulphide exists in which two hydrogen atoms are united to two sulphur atoms; but in this molecule the two sulphur atoms are united to each other, and each hydrogen atom is united to only one of the sulphur atoms, the four individual atoms forming a chain which may be represented as follows:



One atom of nitrogen can hold three atoms of hydrogen in combination with itself, no more and no less. The molecule thus formed is called ammonia, or hydrogen nitride. No other

molecule composed exclusively of hydrogen and nitrogen and *containing only one nitrogen atom* is possible.

One atom of carbon can hold in direct combination with itself four hydrogen atoms, and no other saturated molecule composed exclusively of carbon and hydrogen and *containing only one carbon atom* is possible; nor is any binary compound of carbon and hydrogen possible containing more than one carbon atom, in which each carbon atom is directly and exclusively united to the hydrogen atoms, **for one atom of hydrogen can in no case be united directly to more than one other atom.**

From these facts it is apparent that chlorine, sulphur, nitrogen and carbon have, respectively, different **atomic combining values.**

**153.** The *oxygen* atom unites with two hydrogen atoms, forming the molecule of water, which is the hydroxide (or the normal oxide) of hydrogen. No other saturated compound or molecule composed exclusively of hydrogen and oxygen is possible in which all of the hydrogen is directly united to all of the oxygen. The molecule of water may be represented as  $\text{H}-\text{O}-\text{H}$ .

[The compound called hydrogen dioxide is  $\text{H}-\text{O}-\text{O}-\text{H}$ , in which it will be seen that each hydrogen atom is directly united to only one of the oxygen atoms.]

The oxygen atom must, therefore, have the same combining value in  $\text{H}_2\text{O}$ , or  $\text{H}-\text{O}-\text{H}$ , as the sulphur atom has in  $\text{H}_2\text{S}$ , or  $\text{H}-\text{S}-\text{H}$ .

To satisfy one atom of osmium by saturating its chemical combining power with oxygen requires *four* atoms of oxygen; it requires *three* atoms of oxygen to fully saturate or exhaust the combining power of one atom of sulphur; *two* atoms of oxygen completely saturate one carbon atom; and *one* oxygen atom satisfies one atom of zinc.

*One* oxygen atom combines with two atoms of silver in the formation of argentic oxide; *three* atoms of oxygen are required to satisfy two atoms of aluminum; *five* atoms of oxygen are necessary to form the highest oxide with two atoms of phosphorus; and *seven* atoms of oxygen combine with two atoms of manganese to form permanganic anhydride.

**154.** The potassium atom satisfies but *one* chlorine atom; barium *two*; aluminum *three*; silicon *four*; the phosphorus atom can hold *five* chlorine atoms in combination, forming phosphorus

pentachloride; and one atom of tungsten can unite with *six* chlorine atoms.

**155.** The number of atoms of any one kind which can be held in combination by a given number of atoms of any one other kind is, as evidenced by the foregoing facts, subject to law.

But while the number of *hydrogen* atoms which can be held in combination by a single atom of any one other element is a constant number, the number of atoms of *oxygen*, sulphur or chlorine which can be held in combination by a given number of atoms of any one other element is *not* always constant.

One carbon atom can not hold in combination more than two oxygen atoms; but it forms one compound with two oxygen atoms and another with but one oxygen atom; one atom of sulphur may unite with three oxygen atoms to form sulphur trioxide, but the molecule of sulphur dioxide is composed of one sulphur atom united to only two oxygen atoms; one iron atom can unite with two chlorine atoms to form ferrous chloride, or with three chlorine atoms to form ferric chloride; mercury forms two different oxides and two different chlorides; nitrogen forms five different oxides; and manganese combines with oxygen in seven different proportions.

**156.** The individual combining value of one atom of any given element as compared with the combining value of one atom of any other given element is called its **valence**.

It is also called the combining power, or saturation value, or saturating capacity, or valency, or quantivalence, of the element.

**157.** Valence has no fixed ratio to the relative *masses* of the atoms, nor to the relative *intensity* of their combining energy, but only to the *number* of atoms of one kind required to satisfy the combining power of a given number of atoms of another kind.

Thus the valence of any element is the relative number of individual atoms of any other kind which can be held directly in combination by a given number of atoms of that element.

**158.** Valence is accordingly expressed in units, or in terms referring to the relative numbers of individual atoms capable of entering into direct combination with each other. These units are called *valence units* or *combining units*.

No one single atom possesses more than eight times the valence of any other atom. Hence all atoms of the lowest valence are said to possess a combining value of 1, and atoms of the highest

valence are said to have 8 combining units. Other atoms possess either 2, 3, 4, 5, 6 or 7 units of valence.

All elements, therefore, may be classified into eight groups according to the maximum valence of their atoms, for all the individual atoms of any one element have, *under the same or exactly similar conditions*, the same valence.

**159.** The valence of any element (and of any compound radical) is generally compared to and expressed in units of the valence of the hydrogen atom.

Thus **the valence of hydrogen is 1, and it is invariable.**

The valence of any radical other than the hydrogen atom is expressed by the number of hydrogen atoms which it equals in combining power, or the number of hydrogen atoms for which it can be exchanged, or the number of hydrogen atoms it is capable of holding in combination.

Because the oxygen atom satisfies two hydrogen atoms the valence of oxygen is 2; the valence of lithium is 1 because one lithium atom equals one hydrogen atom in combining power, so that one lithium atom can take the place of one hydrogen atom in chemical combination; the nitrogen atom being capable of holding three hydrogen atoms in combination to form a binary molecule, the valence of nitrogen in this case is 3; etc.

**160.** Hydrogen was selected as the standard of comparison for the expression of the relative individual combining values of all radicals, elemental and compound, because the hydrogen atom itself has a constant valence; because its valence is as low as that of any other element; and because the "hydrogen valence" of any and every element is constant.

**161.** But the valence of an element is not determined exclusively (nor even principally) by an examination of the structure of its binary\* compound with hydrogen, for a great majority of the elements (the metals) do not combine *directly* with hydrogen.†

The valences of the elements are determined chiefly from the structure of their oxides, because all elements except fluorine combine with oxygen. But their chlorides and sulphides must

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\* Binary compounds are compounds consisting of but two elements.

† The metals are instead usually capable of taking the place of (or being exchanged for) the hydrogen in the molecules of various compounds of other elements.

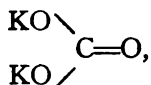
also be examined, and the structure of their binary compounds may be compared with that of compounds containing more than two elements. The oxygen salts are frequently considered in the determination of valence.

**162.** The *hydrogen valence* of an atom is the valence ratio it exhibits in its hydrogen compounds when united by all of its combining power directly or exclusively to hydrogen.

The hydrogen valence of any element is a constant ratio. It never exceeds 4.

**163.** The *oxygen valence* of an element is the valence ratio exhibited by its atom in its oxides and in other compounds in which it is united *directly* to oxygen exclusively, and to other elements only *indirectly* through the mediation of the oxygen.

The oxygen valence of carbon is 2 in CO; it is 4 in CO<sub>2</sub>, and it is 4 also in K<sub>2</sub>CO<sub>3</sub> because the structure of K<sub>2</sub>CO<sub>3</sub> is



in which K has a valence of 1, and O a valence of 2.

The oxygen valence of an element appears in many cases to be subject to variation; it is frequently higher and rarely lower than its hydrogen valence.

The maximum oxygen valence of any element is the highest valence it ever exercises, and as no atom of any other element can saturate more than four oxygen atoms it follows that the highest valence exhibited by any atom is 8, inasmuch as the valence of the oxygen atom itself is 2 because it saturates two hydrogen atoms.

**The valence of the oxygen atom is invariably 2.**

**164.** The *chlorine valence* of an element is the combining value of its atom in its binary compound, or compounds, with *negative* chlorine.

The chlorine valences of a large number of elements, respectively, seem to be variable, and they generally correspond to their respective oxygen valences, except that no atom can have a higher chlorine valence than six.

**The valence of negative chlorine is invariably 1.**

**The valence of positive chlorine is variable.** It may be either 1 or 3 or 5 or 7.

**165.** Whenever atoms exhibit a valence exceeding 6 it is in direct combination with oxygen.

**166.** While the valence of any element is deduced from atomic and molecular weights we can see that the respective combining values of individual atoms of different kinds bear no apparent analogy to their relative atomic weights, for, although the atomic weight of iodine is 126.5 times as great as the weight of an atom of hydrogen, the valence of the hydrogen atom is exactly equal to that of the iodine atom in the only compound formed by these two elements with each other.

**167. Bonds.** The term *bond* is very conveniently employed to express the *unit of valence*.

Thus we say that the hydrogen atom has one bond, the oxygen atom has two bonds, boron has three bonds, carbon has four bonds, nitrogen in nitric acid and other nitrates has five bonds, tungsten in its hexachloride has six bonds, the manganese atom in the permanganates has seven bonds, and osmium in  $\text{OsO}_4$  has eight bonds.

But the use of the term "bond" (or "bonds") should not be permitted to convey the idea that atoms are possessed of links, or ligaments, arms, projections, handles, or points of attachment by which they may be united to each other. The term *bond* is used purely in a figurative sense, and, when used with that distinct understanding it is so terse, expressive, and easily comprehended that its utility amply warrants its employment.

**168.** Pictorially (and only figuratively) we may represent the supposed structure of molecules by the use of the chemical symbols of their elements together with lines appended to those symbols, these lines being used to represent the number of valence units or bonds of each atom, thus:

H is the symbol which represents an atom of hydrogen. H— represents one atom of hydrogen as having one bond, or as having a valence of 1. H—H represents two hydrogen atoms linked to each other, or joined together by their one bond from each atom to form one molecule of hydrogen.

O represents one atom of oxygen. O=, or —O—, represents one atom of oxygen as having two combining units or bonds, or a valence of 2. And O=O represents two oxygen atoms joined together by two bonds from each to form one molecule of oxygen.

The molecule of water is composed of two atoms of hydrogen and one atom of oxygen. It is represented by the formula  $H_2O$ . But to show that the respective combining values of the hydrogen and oxygen are balanced, or mutually satisfied, we may write  $H-O-H$ , which shows that the one oxygen atom with its two bonds is united by one of its valence units to one of the hydrogen atoms and by the remaining valence unit to the other hydrogen atom.

The graphic expression  $H-O-O-H$  represents one molecule of hydrogen dioxide ( $H_2O_2$ ).

A molecule of ozone, composed of three atoms of oxygen, may be represented as



The combination of atoms by means of their valence units or bonds, as represented, is called **atomic linking**.

**169.** The *maximum valence* of an element is sometimes referred to as its *true valence*.

The *ruling valence* of any element is its valence in its most common, simple, and comparatively stable compounds.

The *apparent valence* of any element is the number of bonds or combining units apparently possessed by each of its atoms as inferred from the empiric molecular formula of any one of its compounds. The apparent valence of many of the elements may differ in different compounds.

The *actual valence* of an atom in any particular compound is the number of its combining units actually occupied by combination with any other element or elements. The actual valence of any atom in any one given compound is constant, but may differ from the actual valence of the same element in other compounds.

The ruling actual valence of any element in each particular class or group of its most common and comparatively stable compounds is of the greatest importance, and the student must learn it.

**170.** Atoms and compound radicals having an even number of bonds are called *artiads*; those having an uneven number of bonds are called *perissads*.

Elements having a valence of 1 are called monads.

Elements having a valence of 2 are called dyads.

Elements having a valence of 3 are called triads.

Elements having a valence of 4 are called tetrads.

Elements having a valence of 5 are called pentads.

Elements having a valence of 6 are called hexads.

Elements having a valence of 7 are called heptads.

Elements having a valence of 8 are called octads.

Monad radicals are univalent.

Dyad radicals are bivalent.

Triad radicals are trivalent.

Tetrad radicals are quadrivalent.

Pentad radicals are quinquivalent.

Hexad radicals are sexivalent.

Heptad radicals are septivalent.

Octad radicals are octivalent.

171. It follows from the theory of valence, and is rendered clear by the representation of valence units by means of bonds; that a monad atom can be directly connected with only one other element since it has only one bond; that a dyad atom may act as a link between two other atoms or radicals, since it has two bonds; that a triad may be the center of attachment between two or three other atoms; that tetrads may be connected directly with two, three or four other radicals, etc.

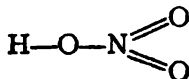
Consistently with these conclusions we would write HOH instead of  $H_2O$ ; HOCl instead of HClO; OBiCl instead of BiOCl;  $H_3CCl$  instead of  $CH_3Cl$ ; KOH instead of KHO;  $H_4NCl$  instead of  $NH_4Cl$ ; but we should then also write  $(KO)_2SO_2$  instead of  $K_2SO_4$ . The most significant molecular formula is that which shows the interatomic linking by which the molecule is held together into one whole system.

172. Many elements exhibit two or more valence ratios.

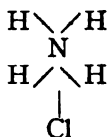
The causes of this apparent **variable valence** are unknown.

A most striking example of variable valence is that of nitrogen, for in the molecule of ammonia one atom of nitrogen is united to and saturated by three hydrogen atoms, so that the nitrogen atom in that compound apparently has a combining power represented by three units; but in nitric acid the nitrogen is evidently a pentad for one atom of nitrogen is there united by its five bonds to three oxygen atoms, the sixth oxygen bond being united to the hydrogen atom, as may be understood from the formula  $HNO_3$ , in which H stands for hydrogen which has 1 bond, N for

nitrogen which has five bonds, and  $O_3$  for three atoms of oxygen each atom of which has two bonds. To show how the atoms are connected or united to and with each other in that molecule we may write it:



In ammonium chloride, also, the nitrogen atom evidently must have five bonds for it is united to four hydrogen atoms and one chlorine atom, as may be seen from the following graphic representation:



But the molecule of nitric oxide consists of one nitrogen atom and one oxygen atom. Hence, in that compound the nitrogen atom is united to the oxygen atom by only two bonds for the valence of oxygen is invariably 2.

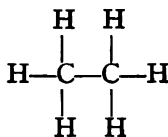
Other examples of variable valence are furnished by sulphur. The sulphur atom is clearly a dyad in hydrogen sulphide,  $H_2S$ , composed of two hydrogen atoms united to one sulphur atom; but it is a tetrad in sulphur dioxide,  $SO_2$ , composed of one sulphur atom and two oxygen atoms, and a hexad in sulphur trioxide,  $SO_3$ , composed of one sulphur atom and three oxygen atoms.

The valence of negative radicals is invariable.

173. Many cases of so-called "variable valence" are only apparent.

The molecular formula for hydrogen dioxide is  $H_2O_2$ , which *apparently* indicates that hydrogen is a dyad, whereas in the molecular formula for water,  $H_2O$ , it is seen that the hydrogen is a monad. But the so-called hydrogen dioxide is in reality composed of two hydroxyl groups; the radical called hydroxyl is  $HO$ , and the molecular formula for hydrogen dioxide would better be written  $(HO)_2$  or  $HO.OH$ . In the last formula we can readily see that the hydrogen atoms are univalent.

The molecule  $C_2H_6$  would seem to show that the valence of carbon is three times that of hydrogen; but the structure of that molecule is more correctly represented by the graphic formula—



which shows that each carbon atom has four bonds instead of only three, the two carbon atoms being united to each other by one combining unit from each atom.

**174.** Temperature seems in many cases to affect the valence of elements.

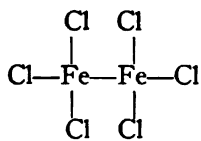
High heat may accomplish not only the decomposition of molecules, but at the same time a reduction of valence of one of the component elements.

The molecular weights of elements as well as of compounds are the sums of the atomic weights of the component atoms, and as the molecular weight of any substance is represented by twice the number expressing its density in the gaseous state as compared to the density of hydrogen, it follows that the valence of elements may be verified by the vapor density.

But the vapor densities of certain substances have been found to split in two at very high temperatures, indicating that the molecules of the gases have been also split in two. By this means the conclusion has been reached that iodine molecules in the gaseous state are diatomic below  $500^{\circ}$  C. but monatomic at  $1570^{\circ}$ . dissociation beginning at  $500^{\circ}$  and being completed at  $1570^{\circ}$ .

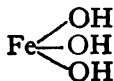
Ferric chloride has heretofore been regarded under all conditions as being composed of two iron atoms and six chlorine atoms, and the molecular formula written  $\text{Fe}_2\text{Cl}_6$ . Its vapor density below  $700^{\circ}$  seems to confirm the correctness of that formula; but at higher temperatures each molecule of  $\text{Fe}_2\text{Cl}_6$  splits up into two molecules of  $\text{FeCl}_3$ .

The formula  $\text{Fe}_2\text{Cl}_6$  has been explained and reconciled with the artiad valence of iron in ferrous compounds (as in  $\text{FeCl}_2$ ) by representing it as—



but this explanation falls in view of the existence of  $\text{FeCl}_3$ .

It is impossible to write a structural formula for ferric hydroxide on the supposition that iron is a triad and yet that the molecule contains more than one iron atom; it must be:

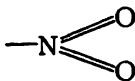


The molecular weight of nitric oxide (NO), as deduced from its vapor density, indicates that its molecule consists of one nitrogen atom and one oxygen atom. Before the molecular formula had been corrected with reference to the vapor density of this compound, it was written  $\text{N}_2\text{O}_2$ . The formula  $\text{N}_2\text{O}_2$  might be said to represent  $\text{O}=\text{N}-\text{N}=\text{O}$ , or  $\text{N}-\text{O}-\text{O}-\text{N}$ , or



but NO can not be reconciled with the assumption that nitrogen is a perissad unless it be admitted that NO is an unsaturated molecule,  $\equiv\text{N}=\text{O}$ , and this admission seems unavoidable in view of the vapor density even at very low temperatures.

Nitrogen tetroxide,  $\text{N}_2\text{O}_4$ , exists only below  $150^\circ \text{C}$ . and splits up into molecules of  $\text{NO}_2$  at higher temperatures. This  $\text{NO}_2$  is probably another unsaturated molecule,



in which the maximum *potential valence* of N may well be 5, although its *actual valence* is 4.

When potassium chlorate,  $\text{KClO}_3$ , is strongly heated it is reduced to  $\text{KCl}$ , all of the oxygen being expelled from the molecule. It will be seen that in this dissociation and reduction the valence of the chlorine, which in  $\text{KClO}_3$  must be 5, is reduced to 1 in  $\text{KCl}$ , while at the same time the polarity of that element, which in  $\text{KClO}_3$  is positive, is changed to negative in  $\text{KCl}$ .

To show that the chlorine is a pentad in  $\text{KClO}_3$ , that molecule might be written  $\text{KOCIO}_2$ , which is also more nearly correct in view of the fact that the K is *not* united directly to the chlorine, but *is* directly united to one of the oxygen atoms.

**175.** The valence of any compound radical is constant. Each particular compound radical in actual combination has under all circumstances uniformly the same number of bonds.

The valence of any compound radical composed of *two* elements, whenever the tied bonds of one element are directly united to those of the other element, is the difference between the number of bonds presented by the two elements, respectively. It is thus found by deducting the sum of the bonds of one from the sum of the bonds of the other element.

The valence of  $\text{CO}_3$  is 2 because C has 4 bonds and  $\text{O}_3$  has  $3 \times 2$ , or 6 bonds.

The valence of the compound radical  $\text{NO}_3$  is 1, because the nitrogen atom has 5 bonds and the three oxygen atoms have 6 bonds together.

The radical  $\text{SO}_4$  has a valence of 2 because the S has 6 bonds and the four oxygen atoms have a total of 8 bonds.

The valence of  $\text{PO}_4$  is 3, because phosphorus, P, is quinquivalent while the oxygen is bivalent, so that the bonds of P are 5 and the bonds of  $\text{O}_4$  are 8.

$\text{CH}_3$  is univalent, because its valence is  $4-3$ .

$\text{CH}_2$  is bivalent for its valence is  $4-2$ .

CH has a valence of 3 because carbon is a tetrad and hydrogen a monad.

The radical CN is a monad for it has one free carbon bond, the carbon atom having 4 bonds and the negative nitrogen atom 3.

**176.** But when a radical composed of two elements contains two or more atoms of one kind (two or more atoms of one element) *tied to each other* instead of to the atom or atoms of the other element, then the valence of that compound radical is *not* to be found by deducting the total bonds of one element from the total bonds of the other. The valence of  $\text{C}_2\text{H}_5$  is not 3, but only 1, because the two carbon atoms are directly united to each other by one bond from each atom, leaving 6 carbon bonds of which 5 are united to the hydrogen atoms, so that only one carbon bond can unite the group to another atom or atomic group.

**177.** All the unused bonds of any compound radical proceed from but one single element in the atomic group constituting that radical.

This fact determines the polarity as well as the valence of compound radicals. All acid-residues of the hydroxyl acids

exercise negative polarity because the bonds by which they hold other radicals are always oxygen bonds.

**178.** But the valence of any radical is not a measure of the quantity of its chemical energy, for chemical energy is that which produces atomic motion and is convertible in other forms of energy.

The valence and polarity of any atom are dependent upon the atom or atoms with which it is in combination (Chapter IX).

The intensity of chemical energy generally diminishes as valence increases.

Univalent elements are generally more energetic in their chemism than the bivalent.

The most decidedly energetic negative elemental radicals are the halogens, and the elements of the oxygen and sulphur group stand next.

The most decidedly energetic positive elements are the alkali metals, and, next, the alkaline earth metals.

Compounds formed by the elements in the exercise of their maximum valence are often less stable than the compounds formed by the same elements with a lower valence.

**179.** In most instances of variable valence the variations are differences of two bonds, as may be seen in comparing the following molecular formulas:  $\text{SO}_2$  and  $\text{SO}_3$ ;  $\text{H}_3\text{P}$  and  $\text{P}_2\text{O}_5$ ;  $\text{H}_3\text{N}$  and  $\text{HONO}_2$ ;  $\text{CO}$  and  $\text{CO}_2$ ;  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_5$ ;  $\text{KOCIO}_2$  and  $\text{KOCIO}_3$ .

**180.** These differences of two bonds, whereby a heptad may in other compounds appear as a pentad, or a pentad as a triad or a monad, and whereby an element may be either a hexad, a tetrad or a dyad, have been represented as arising from the *pairing off* or *mutual saturation* of the combining units or bonds of the same atom. If this assumption were sustained by all the facts it might be thought to explain many cases of variable valence, for if two bonds of an atom having a maximum valence of 7 should mutually satisfy each other by uniting, only 5 bonds would remain, the similar union of another pair of the bonds would convert the same atom into a triad, and the removal of a third pair by the same mode of self-saturation would leave a univalent atom. A sexivalent atom could in the same way become a quadrivalent one, a tetrad could become a dyad, and a monatomic molecule consisting of a bivalent atom might be regarded as a saturated molecule

in which the combining power of each bond is satisfied by the combining power of the other.

This assumption might easily have grown out of the use of the term bond to represent the unit of valence, and out of the use of such expressions as "free bonds" to indicate unused or simply potential valence units, and of the expression "tied bonds" to indicate saturated combining units.

But the theory of the elimination of combining units by pairing must be false for it can not account for such instances of variable valence as are shown in the following comparisons:

NO and  $N_2O_3$ .  
 $FeCl_2$  and  $FeCl_3$ .  
 $HgCl$  and  $HgCl_2$ .  
CO and  $CO_2$ .  
 $H_2O$  and  $H_2O_2$ .

In each of the first three of these examples it will be seen that the valence of one element has changed from odd to even or from even to odd, which could not result from a pairing of bonds.

It is more probable that such molecules as NO and CO are "unsaturated molecules."

Positive nitrogen has a valence of 3 or 5, and the NO may be represented as  $\text{—N=O}$ , having one unused or potential nitrogen combining unit; or it may even be regarded as  $\equiv\text{N=O}$ , having three unused nitrogen combining units.

Carbon has a ruling valence of 4, and CO is, perhaps,  $\text{=C=O}$ , having two unused carbon combining units.

Both NO and CO are recognized as frequently occurring *radicals* in molecules of organic substances, and both are comparatively unstable, having a tendency to enter into combination with other radicals. Thus they are *not saturated molecules*.

181. The valence of which we have thus far treated takes no account of polarity.

It is the valence always referred to in the use of the terms monad, dyad, triad, tetrad, pentad, hexad, heptad and octad, and the terms univalent, bivalent, trivalent, quadrivalent, quinquivalent, sexivalent, septivalent and octivalent.

As the valence of an element is measured according to the number of monad atoms which can be held in combination by one atom of that element, it is expressed by the number of bonds or

combining units of one atom whether that atom exercise positive or negative polarity, or both.

*Hence the valence of any element expresses only the individual numerical saturating power of its atom without regard to its polarity\**

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\* Professor Otis C. Johnson of the University of Michigan uses the term "structural valence" to signify the number of bonds of any atom without regard to polarity, and the term "oxidation valence" to signify the algebraic sum of the positive and negative valence units of any atom in combination. But the structure of a molecule depends upon both polarity and valence. Hence the author of this book uses the term "valence" in its well established sense, to express the total number of bonds of any atom without reference to polarity, and the term "polarity-value" to express the algebraic sum of the positive and negative valence units. (See Chapter IX.)

## CHAPTER IX.

### ATOMIC POLARITY-VALUE.

**182.** All free atoms may be regarded as endowed with *potential* chemical polarity, which, when excited to activity, may become either positive or negative, or both.

The kind and degree of the combining power of any atom (both polarity and valence) apparently depend, at least in part, upon their excitants.

**No atom can possess either polarity or valence irrespective of other atoms.**

Chemical attraction is reciprocal; no atom can alone exercise it or be subject to it, and it is operative only as the result of actual contact between the atoms which mutually attract and combine with each other.

**183.** A single uncombined chlorine atom can have neither positive nor negative polarity, and its actual combining value must be zero. But that chlorine atom becomes negative and exercises a valence of 1 when it enters into combination with one atom of hydrogen. When the same chlorine atom enters into the formation of the molecule  $\text{KOC}\text{l}$  it also exercises a valence of 1, but its polarity in this case becomes positive. If, now, the  $\text{KOC}\text{l}$  be converted into  $\text{KClO}_3$  (or  $\text{KOC}\text{lO}_2$ ) we see that the chlorine atom has assumed a valence of 5 and that its polarity is still positive. But when the  $\text{KClO}_3$  is heated so as to be converted into  $\text{KCl}$  and  $3\text{O}$ , the chlorine atom in the  $\text{KCl}$  is a negative monad.

**184.** Calcium has a valence of 2, and oxygen also has the same individual numerical valence. But calcium invariably exercises positive polarity in its compounds, whereas oxygen is invariably of negative polarity. This difference is a radical one.

**185.** To indicate the difference between the combining power of the chlorine atom in  $\text{HCl}$  and that of the chlorine atom in  $\text{KOC}\text{l}$ , and the difference between the combining power or value of the calcium atom and that of the oxygen atom, the combining units endowed with positive polarity are called **positive bonds** and are treated as *plus* quantities, while the units of atomic com-

binning value having negative polarity are called **negative bonds** and are counted as *minus* quantities.

**186.** To express at once both the quality and the quantity of the combining power of any atom the bonds in actual combination are counted according to their polarity as well as their number.

The quality and quantity of the actual combining value of an atom exercising exclusively positive polarity, or having only positive bonds, must be expressed by the number of its occupied bonds designated as a plus quantity, and the quality and quantity of the actual combining value of an atom exercising exclusively negative polarity, or having only negative bonds, must be expressed by the number of its occupied bonds designated as a minus quantity; but whenever any atom exercises partly positive and partly negative polarity, or when it has both positive bonds and negative bonds, the quality and quantity of its actual combining value must be measured and expressed, not by the *arithmetical sum* of its bonds, but by the *algebraic sum* of its positive and negative bonds.

Thus the real combining value of the calcium atom in  $\text{CaO}$  is not fully expressed by the number 2, but by  $+2$ ; the real combining value of the oxygen atom in  $\text{CaO}$  is not fully expressed by 2, but by  $-2$ ; the real combining value of the chlorine atom in  $\text{HCl}$  is  $-1$ , and that of the chlorine atom in  $\text{KOCl}$  is  $+1$ ; and the real combining value of the nitrogen in  $\text{H}_4\text{NCl}$  is not 5, but the algebraic sum of  $-4$  and  $+1$ , which is  $-3$ .

**187.** The polarity-value of any combined atom is its real combining value as expressed by the algebraic sum of its positive and negative bonds in actual combination.

The polarity-value of a combined atom is a plus quantity whenever that atom exercises only positive polarity, or whenever its positive bonds exceed in number its negative bonds.

The polarity-value of a combined atom is a minus quantity whenever that atom exercises only negative polarity, or whenever its negative bonds exceed in number its positive bonds.

The polarity-value of an atom is zero whenever it has no occupied bonds (i. e., when the atom is free or uncombined), or whenever its positive bonds and its negative bonds are equal numbers (or, in other words, when the algebraic sum of its positive and negative bonds is zero).

**188.** The polarity-value exercised by any atom in any compound depends upon the atom or atoms with which it is *directly* combined.

Chlorine can not have any other polarity-value than  $-1$  in its combination with any element except oxygen; but when the chlorine atom is directly united to oxygen it may have a value of either  $+1$ , or  $+3$ , or  $+5$ , or  $+7$ .

The highest polarity-value ever attained by any atom is the highest valence which it exercises in direct combination with oxygen.

The lowest polarity-value ever attained by any atom is that which it exercises in its binary compound with hydrogen or with any other element exercising positive polarity.

The hydrogen atom excites negative polarity in all other kinds of atoms with which it enters into direct combination because its own chemical polarity is invariably positive.

The oxygen atom excites positive polarity in all other kinds of atoms with which it enters into direct combination because its own chemical polarity is negative.

Thus hydrogen excites negative polarity in chlorine atoms; but oxygen excites positive polarity in them.

Whenever carbon atoms and chlorine atoms are brought into contact so as to combine with each other, the carbon atoms excite negative chemical polarity in the chlorine atoms, and the chlorine atoms excite positive polarity in the carbon atoms.

**189.** The lowest polarity-value which any atom can assume is  $-4$ .

The highest polarity-value possible to any atom is  $+8$ .

The difference between  $-4$  and  $+8$  is a difference of 12 units.

But the difference between the highest and the lowest atomic polarity-value of any one given element never exceeds 8 units.

The negative polarity-value of the carbon atom in its saturated hydrogen compound is  $-4$ , and the polarity-value of osmium in  $\text{OsO}_4$  is  $+8$  — a range of 12 units.

But as the range of possible variation in the polarity-value of any one element is not 12 but 8, it follows that the carbon atom which can have a negative polarity-value of  $-4$  can have no higher positive polarity-value than  $+4$ ; and because the polarity-value of osmium is as high as  $+8$  it could not assume negative chemical polarity at all.

Nitrogen, because it has a negative polarity-value of  $-3$ , can have no higher positive polarity-value than  $+5$ .

Sulphur, because it has a lowest polarity-value of  $-2$ , has a highest polarity-value of  $+6$ .\*

Chlorine, because its lowest atomic polarity-value is  $-1$ , can have a highest polarity-value of  $+7$ .

Per contra, as the chlorine atom saturates one hydrogen atom, it must be able to saturate seven valence units of oxygen, and the molecule  $\text{Cl}_2\text{O}_7$  shows that it does so, for each oxygen atom has two valence units.

As the sulphur atom saturates two hydrogen units, its maximum capacity to saturate oxygen must be six units, as is shown to be the case in  $\text{SO}_3$ .

The highest oxide of nitrogen being  $\text{N}_2\text{O}_5$ , the oxygen valence of that element is 5 and as the difference between 5 and 8 is 3, the nitrogen atom should have a valence of 3 in its hydrogen compound, and we see that it is so, for the molecule of ammonia is  $\text{H}_3\text{N}$ .

As carbon forms the saturated hydrocarbon  $\text{H}_4\text{C}$  it follows that the highest oxide of carbon must contain two oxygen atoms possessing 4 valence units together; therefore its saturated oxide is  $\text{CO}_2$ .

This rule applies to all elements capable of forming both oxygen compounds and hydrogen compounds.

**190.** The highest polarity-value to which chlorine can excite an atom of any other element is  $+6$ .

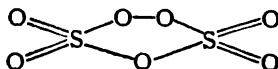
The highest polarity-value to which oxygen can excite any other element is  $+8$ .

The lowest polarity-value to which hydrogen can excite an atom of any other element is  $-4$ .

The polarity-value induced by chlorine is  $+6$  in tungsten,  $+5$

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\* An "oxide of sulphur" having the supposed formula  $\text{S}_2\text{O}_7$  has been announced, about which little is known. If none of the oxygen atoms in the molecule are united directly to each other, then this formula would indicate that sulphur can have a polarity value of  $+7$ . But a molecule composed of two sulphur atoms and seven oxygen atoms may have the structure



in phosphorus, +4 in carbon, +3 in aluminum, +2 in barium, and +1 in hydrogen.

The measure of the maximum polarity-value induced by oxygen is +8 in ruthenium, +7 in iodine, +6 in selenium, +5 in arsenic, +4 in tin, +3 in boron, +2 in calcium, and +1 in silver.

The polarity-value induced by hydrogen is invariably -4 in silicon, -3 in nitrogen, -2 in sulphur, and -1 in bromine.

**191.** When a carbon atom is free or uncombined, its polarity and actual valence are zero; but in its combination with four hydrogen atoms the carbon atom has a polarity-value of -4, while in the formation of  $\text{CO}_2$  the carbon atom has a polarity-value of +4.

Silicon has a polarity-value of +4 in  $\text{SiO}_2$  and of -4 in  $\text{H}_4\text{Si}$ ; its polarity-value in the free state is 0.

Nitrogen has a polarity-value of +3 in nitrites and of -3 in nitrides; its polarity-value in the free state is 0.

Phosphorus in phosphides has a polarity-value of -3, but in phosphites of +3; arsenic in arsenides has a polarity-value of -3, but its value in arsenites is +3; the polarity-value of antimony is -3 in antimonides, but +3 in antimonites; the polarity-value of sulphur in sulphides is -2, but in hyposulphurous acid ( $\text{H}_2\text{SO}_2$ ) it is +2.

**192.** An element exercising positive polarity may have a variable valence; but the negative polarity-value of any element except carbon appears to be constant.

The polarity-value of carbon is, however, invariably -4 in any binary carbon compound containing only one single carbon atom.

All the halogens have an invariable polarity-value of -1 and they always exercise negative polarity; the negative polarity-value of oxygen and the elements of the sulphur family is invariably -2; the negative polarity-value of nitrogen, phosphorus, arsenic and antimony is invariably -3; but the negative polarity-value of carbon may be either -4 as in  $\text{H}_4\text{C}$  or -2 as in  $\text{H}_3\text{CBr}$ .

Elements of variable valence and capable of assuming either positive or negative polarity generally have a higher valence when they exercise positive polarity. Thus whenever any two elements of the chlorine family form binary compounds *with each other* one atom of the positive element ~~generally unites~~ with three or five or seven atoms of the negative element; but one atom of the

→ might unite -

negative element can not unite with more than one atom of the positive element of the same family.

**193.** Bonds of opposite chemical polarity cancel each other when directly united.

No two bonds can cancel each other unless they be of opposite chemical polarity.

All of the tied, occupied or combined bonds in any molecule are canceled.

The arithmetical sum of all the bonds in any molecule must be an even number; and the algebraic sum of the units of positive and negative combining value (or of the positive and negative bonds) of all the atoms of any molecule must be 0.

The algebraic expression of the combining value of any molecule, or of any free atom, or of any single combined atom (an artiad) united by one-half of its tied bonds to a positive element, and by the other half of its tied bonds to a negative element, is 0.

Combined atoms of carbon, sulphur and oxygen may thus have a polarity-value of 0.

**194.** From the foregoing statements it will be understood that whenever any two or more atoms of the same element are directly united to each other in any compound molecule, the bonds by which they are thus united cancel each other because they must be of opposite chemical polarities, although the atoms are of the same kind.

It is important to remember this in order to be able to correctly determine the polarity-value of atoms chained to other atoms of the same kind.

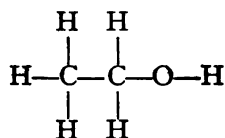
*Valence units* / The polarity-value of each hydrogen atom in  $\text{H}_2\text{O}_2$  is not +2 but +1; but the arithmetical sum of the ~~polarity-values~~ of the two oxygen atoms together is 4 and not 2, because they are chained to each other so that the molecular structure is  $\text{HOOH}$ . One of the oxygen atoms must in this molecule have a polarity-value of 0 while the other has a polarity-value of -2.

The same condition is seen to exist in the molecule  $\text{H}_2\text{S}_2$ .

The direct union of carbon atoms into chains is a common occurrence in organic chemistry, and the polarity-value of carbon atoms chained to each other can be determined only by taking into account the cancellation of the bonds by which they are thus held, each to the other.

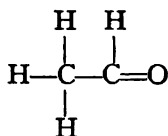
Thus in the molecule of alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ) the polarity-value

of each carbon atom can not be determined by deducting the two oxygen bonds from the six hydrogen bonds, for although the remainder would be 4, showing that the algebraic sum of the polarity-values of the two carbon atoms together must be  $-4$ , the fact would not be shown that each of the carbon atoms has a polarity-value of  $-2$ , which may be the case:



It may be assumed that the alcohol molecule consists of the group  $\text{CH}_3$ , having one *positive* carbon bond by which it is united to  $\text{CH}_2$  which is in turn united to the  $\text{OH}$ . Adopting that view we should find that the carbon atom of the radical  $\text{CH}_3$  must have a polarity-value of  $-2$  (the algebraic sum of  $-3$  and  $+1$ ), and that the carbon atom of the radical  $\text{CH}_2$  must also have a polarity-value of  $-2$ .

But in the molecule of aldehyde:



we must conclude that if the radical  $\text{CH}_3$  acts as a positive monad, as was assumed in the preceding example, then the polarity-value of the second carbon atom must be 0. The algebraic sum of  $-2$  and 0 is  $-2$ , and as the algebraic sum of the polarity-values of all the hydrogen atoms and all the oxygen atoms together is  $+2$ , the two carbon atoms together must furnish just two negative bonds.

The *valence* of every carbon atom in any organic compound is invariably 4; that is, it has 4 bonds. But its polarity-value may be either  $+4$ , or  $+2$ , or 0, or  $-2$ , or  $-4$ .

**195.** The algebraic sum of the polarity-values of all the atoms of any one of the elements in any compound is *found* by deducting from 0 the algebraic sum of the polarity-values of all the atoms of the other elements together.

The following examples illustrate this rule:

The polarity-value of K in  $\text{KClO}_3$  is  $+1$  because the algebraic sum of the polarity-values of Cl and  $\text{O}_3$  in this molecule is  $-1$ , and  $-1$  deducted from 0 leaves  $+1$ .

The polarity-value of the Cl in the same molecule is  $+5$  because the algebraic sum of the polarity-values of the K and the  $\text{O}_3$  is  $-5$  and the remainder obtained by deducting  $-5$  from 0 is  $+5$ .

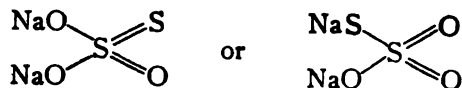
The algebraic sum of the polarity-values of the potassium atoms in  $\text{K}_3\text{C}_6\text{H}_5\text{O}_7$  is  $+3$  because the algebraic sum of the polarity-values of the atoms of the carbon, hydrogen and oxygen in the molecule is  $-3$ .

The algebraic sum of the polarity-values of the six carbon atoms in  $\text{K}_3\text{C}_6\text{H}_5\text{O}_7$  must be  $+6$  because the algebraic sum of the polarity-values of the atoms of potassium, hydrogen and oxygen is  $-6$ .

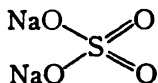
The algebraic sum of the polarity-values of the carbon atoms in  $\text{C}_6\text{H}_{10}\text{O}_5$  is 0; that of the two sulphur atoms in  $\text{Na}_2\text{S}_2\text{O}_3$  is  $+4$ ; that of the boron atoms in  $\text{Na}_2\text{B}_4\text{O}_7$  is  $+12$ ; that of the phosphorus atom in  $\text{H}_2\text{P}_2\text{O}_7$  is  $+1$ ; that of the P in  $\text{H}_2\text{PHO}_3$  is  $+3$ ; that of the As in  $\text{H}_2\text{AsHO}_3$  is  $+3$ .

But to find the polarity-value of *each atom* of one element when more than one atom of that element enters into the composition of the same molecule is not always possible by the method described and illustrated in the preceding paragraph, as may be seen from the following examples.

By the method referred to we find that the algebraic sum of the polarity-values of the two sulphur atoms in  $\text{Na}_2\text{S}_2\text{O}_3$  is  $+4$ ; but it does not follow from this result that each of these two sulphur atoms has a polarity-value of  $+2$ . In fact the polarity-value of one of them is  $+6$  and that of the other is  $-2$ , for the structure of the molecule is



One sulphur atom performs the acidic function and corresponds to the acidic sulphur atom in ordinary sodium sulphate, which is



The second sulphur atom in the sodium thiosulphate,  $\text{Na}_2\text{S}_2\text{O}_3$  (which ought to be written  $\text{Na}_2\text{SO}_3\text{S}$ ) is of negative polarity and performs the function of oxygen.

**196.** A clear conception of the meaning of the term polarity-value, and of the expressions positive and negative bonds, is so important that the student is advised not to leave this subject until he thoroughly understands it. He can not master the art of constructing molecular formulas and of writing and balancing chemical equations unless he is able to determine at a glance the polarity-values of the most common and important elements.

To render clear the difference between valence and polarity-value the following additional illustrations are presented:

We say that the *valence* of sulphur in  $\text{H}_2\text{S}$  is 2, and that its *valence* in  $\text{SO}_2$  is 4. Here is an apparent difference of two combining units, and we call the sulphur atom in  $\text{H}_2\text{S}$  a dyad, whereas the sulphur atom in  $\text{SO}_2$  is called a tetrad. But when we speak of the *polarity-value* of sulphur in  $\text{H}_2\text{S}$  we take into account the fact that the two bonds of the sulphur atom in that molecule are of negative polarity, and for the purpose of expressing that distinction we state its value not as 2, but as  $-2$ . On the other hand the polarity-value of the sulphur in  $\text{SO}_2$  is expressed by  $+4$  because that sulphur atom is of positive polarity. The difference between  $-2$  and  $+4$  is not 2, but 6.

The difference between the *valence* of the sulphur in  $\text{SO}_2$  and the *valence* of the sulphur in  $\text{SO}_3$  is 2, because the sulphur in the former molecule has 4 bonds and in the latter 6 bonds; the *polarity-value* of the sulphur in  $\text{SO}_2$  is  $+4$  and in  $\text{SO}_3$  it is  $+6$ , so that the difference in polarity-value is also 2.

The number of the combining units of the hydrogen and also of the nitrogen in the molecule  $\text{H}_3\text{N}$  is 3. The *arithmetical sum* of the hydrogen bonds and the nitrogen bonds in  $\text{H}_3\text{N}$  is therefore 6. But the *algebraic sum* of the polarity-values of all these bonds is 0, for the hydrogen bonds are positive and the nitrogen bonds negative, and  $+3$  added to  $-3$  makes the sum of 0.

In  $\text{H}_4\text{NCl}$  the four hydrogen atoms have together 4 bonds, the nitrogen atom has 5 bonds, and the chlorine atom 1 bond. But as the hydrogen bonds are positive and the chlorine bonds negative, it follows that four of the nitrogen bonds must be negative, while its fifth bond is positive. The *valence* of the N in

$\text{H}_3\text{N}$  is 3, and in  $\text{H}_4\text{NCl}$  it is 5—a difference of 2; but the *polarity-value* of the N is in both molecules  $-3$ .

When  $\text{H}_3\text{N}$  is converted into a nitrate by oxidation, the nitrogen becomes the acidic element in that nitrate and assumes a polarity-value of  $+5$ . The *difference* between the *valence* of the N in  $\text{H}_3\text{N}$  and that of the N in  $\text{HNO}_3$  is only 2; but the difference between the *polarity-value* of the N in  $\text{H}_3\text{N}$ , which is  $-3$ , and the polarity-value of the N in  $\text{HNO}_3$ , which is  $+5$ , is not 2, but 8.

The *valence* of the P in  $\text{HPH}_2\text{O}_2$  is 5; but its *polarity-value* is  $+1$ .

The *valence* of the As in  $\text{H}_2\text{AsHO}_3$  is 5; but its *polarity-value* is  $+3$ .

The *valence* of the carbon in  $\text{H}_4\text{C}$ , and in  $\text{H}_3\text{CCl}$ , and in  $\text{H}_2\text{CCl}_2$ , and in  $\text{HCCl}_3$ , is 4. But the *polarity-value* of the C in  $\text{H}_4\text{C}$  is  $-4$ ; in  $\text{H}_3\text{CCl}$  it is  $-2$ , in  $\text{H}_2\text{CCl}_2$  it is 0, and in  $\text{HCCl}_3$  it is  $+2$ .\*

**197.** The student should thoroughly learn the following summary of the facts already presented in relation to atomic polarity-value:

I. *Hydrogen* is of positive polarity with regard to all other elements. Its polarity-value is invariably  $+1$ .

II. Any other element united directly to hydrogen must, therefore, and to that extent, be of negative polarity, and all bonds united to hydrogen bonds are negative.

III. *Oxygen* is of negative polarity with regard to all other elements, and its polarity-value is invariably  $-2$ .

IV. Any other element united directly to oxygen must, therefore, and to that extent, have positive polarity, and all bonds united to oxygen are positive.

V. In any metallic compound the metal is of positive polarity (except quasi-metals, like arsenic, when united to hydrogen).

VI. Any element (except hydrogen) united directly to a metal must, therefore, and to that extent, be of negative polarity, and all bonds (except hydrogen bonds) united to any metal are negative bonds.

VII. *Chlorine* is of negative polarity in all chlorides, and

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\* The illustrations here used are largely taken from *Qualitative Chemical Analysis* by Albert B. Prescott, Ph. D., and Otis C. Johnson, A. M., University of Michigan, published by D. Van Nostrand Co., New York.

its polarity-value is then invariably  $-1$ ; in chlorates the polarity-value of the chlorine is  $+5$ .

VIII. The polarity-value of *sulphur* in all sulphides is  $-2$ ; in all sulphates it is  $+6$ , and in all sulphites  $+4$ .

IX. The polarity-value of *nitrogen* in ammonia and all ammonium compounds is  $-3$ ; in nitric acid and other nitrates it is  $+5$ ; and in nitrites it is  $+3$ .

X. Single atoms of carbon and nitrogen may have both positive and negative bonds at the same time.

## CHAPTER X.

### CHEMICAL NOTATION.

**198.** In the preceding chapters we have already made use of several chemical symbols and formulas. Before proceeding further it is necessary that the student learn the principles of the system of chemical notation.

An understanding of the constitution of matter, and of the chemical changes to which matter is subject, would be scarcely possible without some method of graphic representation on paper. Therefore a written language and nomenclature of chemistry, as well as a method of chemical mathematics, must be employed in order to elucidate, systematize, and supplement the successful performance of actual experimentation and work.

Useful results in the pursuit of the study of chemistry are unattainable without the combination and alternation of theory and practice, philosophy and performance. Laboratory work, study, the writing of formulas and equations, the solution of problems in chemical notation and arithmetic, must go together.

**199.** In order to represent at a glance the composition and structure of molecules, a system of chemical notation was invented by Berzelius, which has been modified and adapted by other chemists to correspond with the development of chemistry since his day.

**Chemical notation** is a system of representing atoms and molecules by means of symbols and formulas.

**200.** Each atom of any given element is represented by a specific symbol.

No two different kinds of atoms are represented by the same symbol.

The **symbols** used consist of letters. These letters are the single initials of the latinic or other names of the elements, or the initial letter accompanied by one additional letter in some cases where the latinic names of two or more elements begin with the same letter.

**201.** The symbols of the more common elements, and their derivation, are shown in the following table:\*

<i>English Name of the Element.</i>	<i>Latinic Name of the Element.</i>	<i>Symbol Derived from the Latinic Name.</i>
Aluminum	Aluminum	Al
Antimony	Stibium	Sb
Arsenic	Arsenum	As
Barium	Barium	Ba
Bismuth	Bismuthum	Bi
Boron	Borum	B
Bromine	Bromum	Br
Cadmium	Cadmium	Cd
Calcium	Calcium	Ca
Carbon	Carboneum	C
Chlorine	Chlorum	Cl
Chromium	Chromium	Cr
Copper	Cuprum	Cu
Gold	Aurum	Au
Hydrogen	Hydrogenium	H
Iodine	Iodum	I
Iron	Ferrum	Fe
Lead	Plumbum	Pb
Lithium	Lithium	Li
Magnesium	Magnesium	Mg
Manganese	Manganum	Mn
Mercury	Hydrargyrum	Hg
Nitrogen	Nitrogenium	N
Oxygen	Oxygenium	O
Phosphorus	Phosphorus	P
Potassium	Kalium	K
Silicon	Silicium	Si
Silver	Argentum	Ag
Sodium	Natrium	Na
Strontium	Strontium	Sr
Sulphur	Sulphur	S
Tin	Stannum	Sn
Zinc	Zincum	Zn

**202.** The full meaning of the chemical symbols must be thoroughly understood by the student before he can appreciate the value of chemical notation.

The symbol H stands for not merely the name hydrogen and the element called by that name, but, at the same time, for one atom of hydrogen and its mass or combining weight.

The symbol O means oxygen, and one atom of oxygen, and the combining weight of oxygen.

**203.** Symbolic formulas consist of one or more symbols, to-

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\* The symbols of all elements known are given in the table of atomic weights on pp. 52 and 53.

gether with one or more numerals, or of two or more symbols with or without numerals.

Thus  $\text{HCl}$  is a symbolic formula, for it is composed of two symbols,  $\text{H}$  and  $\text{Cl}$ ;  $\text{H}_2$  is a symbolic formula because it includes a numeral added to the symbol  $\text{H}$ ;  $2\text{H}$  is also a formula for the same reason; and  $\text{HO}$  as well as  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  are symbolic formulas.

**204.** Symbolic formulas may represent a, free atoms; or b, compound radicals; or c, molecules.

a. Formulas for two or more free atoms consist of one symbol preceded by a large numeral, as shown by the following examples:

$2\text{H}$  represents 2 free hydrogen atoms;

$3\text{H}$  represents 3 free hydrogen atoms;

$2\text{O}$  represents 2 free oxygen atoms;

$3\text{O}$  represents 3 free oxygen atoms;

$4\text{P}$  represents 4 free phosphorus atoms.

b. Formulas for compound radicals consist of two or more symbols, with or without accompanying numerals, representing atomic groups in which one element is not completely saturated, which may be known from the respective valences of the kind and number of the atoms of which the group is composed.

The formula  $\text{HO}$  is a symbolic formula for the radical hydroxyl. It is seen not to be the formula of a saturated molecule because  $\text{H}$  and  $\text{O}$  do not have the same valence and hence can not saturate each other, atom for atom.

The formula  $\text{CH}_3$  is seen not to be a formula for a saturated molecule because the carbon atom has 4 bonds, whereas the three hydrogen atoms together present only three bonds;  $\text{CH}_3$  is, therefore, the formula of a radical.

c. The formula  $\text{HCl}$  is a formula for a saturated molecule because  $\text{H}$  and  $\text{Cl}$  have the same valence, and the algebraic sum of their polarity-values is 0.

$\text{H}_2\text{O}$  is also a molecular formula for a saturated compound, for  $\text{H}_2$  and  $\text{O}$  are equivalent;  $\text{CaO}$  is another formula for a saturated molecule, for  $\text{Ca}$  and  $\text{O}$  are both dyads.

**205.** But single symbols, with or without numerals, may also represent molecules.

Zn is the symbol for zinc and stands for one atom of that metal; but Zn also stands for one molecule of zinc, because that molecule is monatomic.

P<sub>4</sub> stands for one molecule of phosphorus, because the phosphorus molecule is tetratomic.

H<sub>2</sub> represents one molecule of hydrogen.

O<sub>2</sub> represents one molecule of oxygen.

O<sub>3</sub> means one molecule of ozone.

**206.** The *numerals* used in symbolic formulas are of two kinds—large and small (“superior” and “inferior,” as the printers would call the type).

Both kinds of numerals are multipliers or co-efficients and apply to the symbols or formulas according to their position.

Large (or “superior”) numerals placed in front of a single symbol multiply that symbol, but they indicate that free atoms are referred to.

Large (or superior) numerals placed in front of atomic groups multiply these whole groups, whether entire molecules or parts of molecules, up to the next following period.

Small (or “inferior”) numerals are always placed *after* the symbols, and to the right of each symbol, and apply only to the symbol to which they are appended.

Thus—

2H means 2 free hydrogen atoms.

3H means 3 free hydrogen atoms.

3HCl means three molecules of hydrochloric acid.

3H<sub>2</sub>O means three molecules of water.

3O means three free oxygen atoms.

O<sub>3</sub> means one molecule of ozone.

3O<sub>3</sub> means three molecules of ozone.

H<sub>2</sub> means one molecule of hydrogen.

3H<sub>2</sub> means three molecules of hydrogen.

Three atoms of hydrogen must be written 3H, and not H<sub>3</sub>.

Two atoms of free hydrogen must not be written H<sub>2</sub>, but 2H.

P<sub>4</sub> stands for one molecule of phosphorus, but 4P stands for four free phosphorus atoms.

**207.** The principles of construction of molecular formulas. Symbolic molecular formulas are based upon the atomic

hypothesis, the theory of chemical polarity, and the theory of valence.

They are based upon the atomic hypothesis because every symbol refers to one atom.

They are based upon the theory of chemical polarity because positive and negative radicals are recognized as composing the molecules, and the positive radicals are placed before the negative radicals in all molecular formulas, so far as possible (or by others the positive radicals are placed *after* the negative radicals in all molecular formulas).

Symbolic molecular formulas are based upon the theory of valence because the structure of molecules is governed and determined by valence.

Water is composed of hydrogen and oxygen. Hydrogen is represented by the symbol H, and oxygen by the symbol O. As H is positive and O negative, we place the symbol H before the symbol O. But as H is a monad, having only one bond, while O is a dyad, or has two bonds, and as all saturated molecules must have the same number of positive bonds as of negative bonds, we must have 2 atoms of H to satisfy one atom of O, and the molecular formula for water (the simplest saturated compound of H and O) must, therefore, be  $H_2O$ .

**208.** Molecular formulas must contain the symbols of all the elements composing the molecules.

If more than one atom of any one of its elements enters into the molecule a small numeral added to and after the symbol is used to indicate the number required.

If one or more compound radicals be recognized as entering into the composition of the molecule, the atomic groups representing such radicals are to be indicated in the molecular formula.

When atomic groups representing compound radicals are written in molecular formulas and require to be multiplied, these atomic groups are enclosed within brackets, and the small numeral necessary to indicate how many times that group or radical is contained in the molecule is placed outside the brackets to the right, thus:

$Ca(OH)_2$  is a formula which shows that the radical hydroxy! is contained in the molecule twice.

$\text{Fe}(\text{OH})_3$  signifies a molecule composed of one iron atom united to 3 times OH.

$(\text{H}_4\text{N})_2\text{SO}_4$  means twice the group  $\text{H}_4\text{N}$  united to the group  $\text{SO}_4$ .

**209.** As it is entirely practicable, convenient, permissible and customary in writing nearly all molecules of inorganic chemical compounds to regard the compound as made up of two radicals (ions) and two only—one positive and the other negative—the molecular formulas are generally constructed accordingly.

**210.** Whenever the molecular formulas of compounds containing three or more elements, or containing at least one compound radical, are written, the symbols are preferably placed in such order as to show how the several radicals, elemental and compound, are united to each other according to their respective valences.

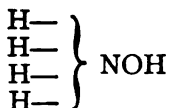
It is, for example, better to write HOH than to write  $\text{H}_2\text{O}$  if it be desired to show how the three atoms are linked to each other, the two monad atoms being united, not directly but indirectly, through the linking function of the dyad.

KOH is preferable to KHO because if K and H were united directly to each other they could no longer be linked to the O since they would have no bonds left; but K can be united to OH, or KO can be united to H, or K and H can each separately be united to the O. We accordingly write KOH to show the actual atomic linking. K and H never unite directly.

The formula  $\text{NH}_4\text{Cl}$  is inconsistent because the N is directly united to the Cl as well as to the  $\text{H}_4$ , and because, moreover, the hydrogen is the only exclusively positive element of the molecule. The formula should instead be written  $\text{H}_4\text{NCl}$ .

HO.OH is a more explicit formula than  $\text{H}_2\text{O}_2$ ; but  $(\text{HO})_2$  might be used.

$\text{NH}_4\text{HO}$  is inconsistent; but  $\text{H}_4\text{NOH}$  is consistent, for the N is united directly to the  $\text{H}_4$  and to the O of the OH, but the H of the OH is *not* united directly to the N, but only to the O, as will be seen in the following graphic expression showing the bonds of all the atoms:



**211.** A large figure or numeral placed *before* any formula applies to all that follows the number up to the first period, except that if the numeral is placed before or after brackets enclosing a formula the number multiplies all that is contained within those brackets.

In  $2K_2CO_3$  the first figure 2 applies to all that follows; the small ("inferior") figure 2 applies only to K; and the small figure 3 applies only to O.

In  $2K_2CO_3 \cdot 3H_2O$  the first figure 2 applies to  $K_2CO_3$  and to nothing further, and the large figure 3 refers to  $H_2O$ .

In  $3(2K_2CO_3 \cdot 3H_2O)$ , and also in  $(2K_2CO_3 \cdot 3H_2O)_3$ , the figure 3 *outside* the brackets, whether before or after, applies to all within the brackets.

In  $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$  the figure 4 applies only to  $MgCO_3$ ; the inferior figure 2 in  $Mg(OH)_2$  applies only to the OH, and the figure 5 applies to  $H_2O$ .

In  $3Pb(C_2H_3O_2)_2$  the large figure 3 in front applies to all that follows, namely to  $Pb(C_2H_3O_2)_2$ .

In  $6(NaC_2H_3O_2 \cdot 3H_2O)$  the figure 6 multiplies all that is placed within the brackets.

In  $Fe_4(P_2O_7)_3 \cdot 4(Na_3C_6H_5O_7) \cdot 8H_2O$  we read that 4 atoms of iron are united to three times  $P_2O_7$ , and that that compound is further combined in some way with four times  $Na_3C_6H_5O_7$  and eight times  $H_2O$ .

**212.** Chemical symbolic formulas are of several kinds:

1. **Empiric formulas** express in the simplest terms the *relative* number of atoms of each kind contained in a compound.

The empiric formula showing the composition of acetic acid is  $CH_2O$ ; it simply indicates that for each carbon atom contained in that acid we have one atom of oxygen and two atoms of hydrogen.

Empiric formulas are not intended to show the absolute number of atoms of each kind in one molecule.

In all empiric formulas of compounds consisting of carbon, hydrogen and oxygen the three elements are always written in the same order—the carbon atoms first, hydrogen next, and oxygen last. Hence such formulas do not indicate the actual relative position of the component atoms, or the interatomic linking.

The formula  $CH_2O$  is the molecular formula of methyl alde-

hyde, or formaldehyde, and at the same time the empiric formula of acetic acid.

2. **Molecular formulas** show not only the relative number of atoms of each kind which enter into the compound, but at the same time the *actual* number of each kind of atoms composing one molecule of it.

The simplest molecular formula of formic aldehyde is  $\text{CH}_2\text{O}$ ; but the simplest molecular formula of acetic acid is  $\text{C}_2\text{H}_4\text{O}_2$ , instead of  $\text{CH}_2\text{O}$ .

But even the molecular formulas as usually written do not always show the relative positions of the atoms within the molecule.

The empiric formula and the molecular formula of the same compound are frequently the same, as in the case of the formic aldehyde; but when the molecular formula differs from the empiric formula of the same compound the molecular formula is, of course, a multiple of the other.

3. A **constitutional** or **structural formula** shows not only the actual number of atoms of each kind contained in one molecule of a compound, but also the probable or actual interatomic linking, or *grouping*, or relative positions of these atoms within the molecule, as far as possible.

The constitutional or structural formula of acetic acid is neither  $\text{CH}_2\text{O}$  nor  $\text{C}_2\text{H}_4\text{O}_2$ , but  $\text{H}_3\text{C.CO.OH}$ , which indicates that the atoms composing the molecule are arranged into three groups, or radicals, which are  $\text{H}_3\text{C}$  (methyl),  $\text{CO}$  (carbonyl), and  $\text{OH}$  (hydroxyl).

213. Polyvalent atoms (or atoms having more than two bonds) necessarily form more complex molecules than the molecules formed by monads or dyads. Hence the molecular formulas of compounds formed by carbon and nitrogen are frequently complicated.

Chains, rings and clusters of atoms occur in both inorganic and organic chemistry; but the most complex structural formulas are those of the molecules of organic substances in which carbon is the ruling element and in which nitrogen, also, not infrequently, occurs. The complex structure of the compounds of carbon and of nitrogen is also due to the fact that these elements may be either positive, or negative, or both.

For the purposes of this book it will be sufficient to give a few

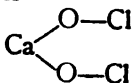
examples of the chains, rings, and clusters which appear to exist in the molecules of inorganic compounds:



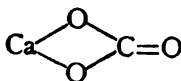
represents the structure of the molecule of ozone, which consists of three oxygen atoms. As each oxygen atom has two bonds, these three atoms are assumed to be linked to each other in such a manner that each is united directly to both of the others, since any other arrangement would be inconceivable.

Potassium cyanide is represented by the structural formula  $\text{K}-\text{C}\equiv\text{N}$ .

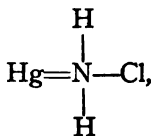
Calcium hypochlorite is



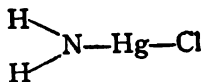
Calcium carbonate is



Mercur-ammonium chloride is

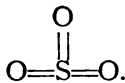


or perhaps

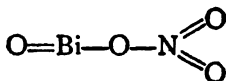


Sulphur dioxide is  $\text{O}=\text{S}=\text{O}$ .

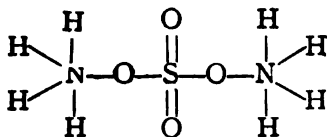
Sulphur trioxide is



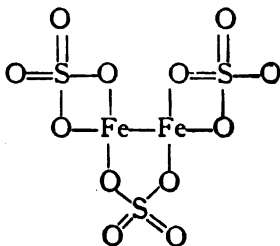
Bismuthyl nitrate, or "subnitrate of bismuth," is



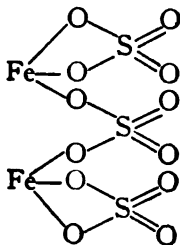
Ammonium sulphate may be represented as:



Ferric sulphate *was* represented as:

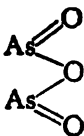


when ferric iron was regarded as a tetrad. But if it be admitted that iron is a triad, as indicated by the apparently demonstrated existence of the molecule  $\text{FeCl}_3$ , then the structural molecular formula of ferric sulphate would have to be represented by:

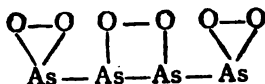


Upon examination of these two formulas for ferric sulphate, the student will see that each iron atom in the first formula is represented as having four bonds, whereas in the second each iron atom has only three bonds.

If the molecule of arsenous oxide is  $\text{As}_2\text{O}_3$ , then its structural expression on paper would be



But if arsenous oxide is  $\text{As}_4\text{O}_6$  instead of  $\text{As}_2\text{O}_3$ , then its atomic linking would have to be represented as:



or by a formula showing the probable (or, at least, the possible) disposition of the bonds of all the atoms in such a way as to connect all of them together in one group while at the same time the assumed valence of each element is not deviated from, nor the theory of chemical polarity violated.

**214.** It will be readily seen that the rational or constitutional structural formulas can not be conveniently employed in writing, because too complex and time-consuming. They are used only when it is desired to indicate the probable interior structure or *constitution* of molecules, or their system of interatomic linking.

But the atoms composing the molecules are, of course, *not in the same plane*, as unavoidably represented on paper. The relative position of the atoms is evidently such that at least the more complex molecules would form geometric figures if the atoms could be connected by straight lines.

[The definite form of the crystal of any crystallizable substance must have an intimate relation to the form of its molecule.]

The principal uses of constitutional formulas are to show the radicals composing the molecules, and which of these radicals are directly united to each other, and to account for all their bonds and their polarities, and it may be remarked here that in organic chemistry the chemical and other properties of many compounds frequently depend upon the grouping of the atoms.

There are different organic chemical compounds having widely different properties, although their molecules are composed of the same elements in the same proportions and contain the same number of atoms of each element, thus differing only as to their linking.

**215.** The **customary molecular formulas** are more simple, and show the recognized groups of atoms which are known or supposed to exist in the molecules, or they show only two radicals, elemental or compound, which may be most conveniently and correctly regarded as characteristic of the molecules represented, and of the classes of compounds to which they belong.

Thus instead of writing the molecular formula of acetic acid  $\text{H}_3\text{C.CO.OH}$  it is almost universally written  $\text{HC}_2\text{H}_3\text{O}_2$ .

The object in view is to show that this compound is a mono-basic acid, or that the one hydrogen atom placed first in the formula may be replaced by any other positive monad while the remainder of the formula—the  $\text{C}_2\text{H}_3\text{O}_2$ —is the “acid-radical” or “acid-residue” characteristic of all acetates, for all acetates, including acetic acid (hydrogen acetate), contain the group  $\text{C}_2\text{H}_3\text{O}_2$ , which is a condensation of  $\text{CH}_3\text{CO.O—}$ , or  $\text{—O.CO.CH}_3$ , a residue obtained by removing the hydrogen atom (H) from the group HO in  $\text{HO.CO.CH}_3$ .

The student may recognize the convenience of this method when we place together the formulas of several acetates, thus:

$\text{HC}_2\text{H}_3\text{O}_2$  = acetic acid (hydrogen acetate).

$\text{KC}_2\text{H}_3\text{O}_2$  = potassium acetate.

$\text{AgC}_2\text{H}_3\text{O}_2$  = silver acetate.

$\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$  = magnesium acetate.

The acetates named in the foregoing group may be written:

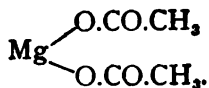
$\text{HOC}_2\text{H}_3\text{O}$  = hydrogen acetate

$\text{KOC}_2\text{H}_3\text{O}$  = potassium acetate

$\text{AgOC}_2\text{H}_3\text{O}$  = silver acetate

$\text{MgO}_2(\text{C}_2\text{H}_3\text{O})_2$  = magnesium acetate

because the molecule of acetic acid (hydrogen acetate) is  $\text{HO.CO.CH}_3$ , potassium acetate is  $\text{KO.CO.CH}_3$ , silver acetate is  $\text{AgO.CO.CH}_3$ , and the magnesium acetate is  $\text{MgO}_2(\text{CO})_2(\text{CH}_3)_2$  or



It will be seen, therefore, that it is the hydroxyl (HO) which is exchanged for KO, or AgO, or

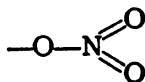


while the  $\text{CO.CH}_3$  remains unchanged, and  $\text{KO.CO.CH}_3$  represents the real structure of potassium acetate. But it may also

be said that only the H of the HO is exchanged, and it is more convenient to write  $KC_2H_3O_2$  than to write  $KOC_2H_3O$ , or  $KO.CO.CH_3$ .

**216.** All ammonium compounds contain the group  $H_4N$  (or  $NH_4$ ); hence that group, being a positive radical, appears *first* in the molecular formulas of all ammonium salts.

All nitrates contain the negative radical  $NO_3$ , which is simply a condensation of



Hence we write  $H_4NNO_3$  (or  $NH_4NO_3$ ), and we can at once see that the formula stands for ammonium nitrate.

The greater convenience of the customary formulas over all others is further illustrated by the following comparisons:

<i>Compound.</i>	<i>Abbreviated Structural formula.</i>	<i>Customary formula.</i>
Silver nitrate	$AgONO_2$	$AgNO_3$
Sodium nitrate	$NaONO_2$	$NaNO_3$
Lead nitrate	$PbO_2(NO_2)_2$	$Pb(NO_3)_2$
Bismuth nitrate	$BiO_3(NO_2)_3$	$Bi(NO_3)_3$
Magnesium sulphate	$MgO_2SO_2$	$MgSO_4$
Potassium sulphate	$(KO)_2SO_2$	$K_2SO_4$
Phosphoric acid	$(HO)_3PO$	$H_3PO_4$
Calcium phosphate	$Ca_3O_6(PO)_2$	$Ca_3(PO_4)_2$

**217.** The most common radicals, elemental and compound, occurring in molecules especially important to pharmaceutical students, together with their symbols, their respective valences in their most common compounds, and the kinds of compounds formed by them, are shown in the following table, in which the positive radicals are indicated by the plus sign and the negative radicals by the minus sign:

<i>Name of Radical.</i>	<i>Symbol.</i>	<i>Number of Bonds.</i>	<i>Compounds Formed By It.</i>
Acetate radical—	$C_2H_3O_2$	I	Acetates.
Aluminic radical+	Al	III	Aluminum compounds.
Ammonium+	$H_4N$	I	Ammonium compounds.
Amyl+	$C_5H_{11}$	I	Amyl compounds
Antimonic radical+	Sb	V	Antimonic compounds.
Antimonous radical+	Sb	III	Antimonous compounds.
Antimonyl+	$SbO$	I	Antimonyl compounds.
Argentie radical+	Ag	I	Argentie compounds.

<i>Name of Radical.</i>	<i>Symbol.</i>	<i>Number of Bonds.</i>	<i>Compounds Formed By It.</i>
Arsenate radical—	AsO <sub>2</sub>	III	Arsenates.
Arsenite radical—	HAsO <sub>2</sub>	II	Arsenites.
Barium+	Ba	II	Barium compounds.
Benzoate radical—	C <sub>6</sub> H <sub>5</sub> O <sub>2</sub>	I	Benzoates.
Bismuthous radical+	Bi	III	Bismuthous compounds.
Bismuthyl+	BiO	I	Bismuthyl compounds.
Borate radical—	BO <sub>2</sub>	III	Borates (normal).
Bromide radical—	Br	I	Bromides.
Cadmium+	Cd	II	Cadmium compounds.
Calcium+	Ca	II	Calcium compounds.
Carbon+	C	IV	Carbon-Hydrogen compounds, etc.
Carbonate radical—	CO <sub>2</sub>	II	Carbonates.
Chlorate radical—	ClO <sub>2</sub>	I	Chlorates.
Chloride radical—	Cl	I	Chlorides.
Chromate radical—	CrO <sub>4</sub>	II	Chromates (normal).
Chromic radical+	Cr	III	Chromic compounds.
Citrate radical—	C <sub>6</sub> H <sub>5</sub> O <sub>7</sub>	III	Citrates.
Cobaltous radical+	Co	II	Cobaltous compounds.
Cupric radical+	Cu	II	Cupric compounds.
Cyanate radical—	OCN	I	Cyanates.
Cyanide radical—	CN	I	Cyanides.
Dichromate radical—	Cr <sub>2</sub> O <sub>7</sub>	II	Dichromates.
Ethyl+	C <sub>2</sub> H <sub>5</sub>	I	Ethyl compounds.
Ferric radical+	Fe	III	Ferric compounds.
Ferrous radical+	Fe	II	Ferrous compounds.
Formiate radical—	COOH	I	Formiates.
Glyceryl+	C <sub>3</sub> H <sub>5</sub>	III	Glyceryl compounds.
Gold+	Au	III	Gold compounds (Trichloride).
Hydrogen+	H	I	Acids, etc.
Hydroxyl—	HO	I	Hydroxides, Acids, Alcohols.
Hypochlorite radical—	ClO	I	Hypochlorites.
Hypophosphite radical—	PH <sub>2</sub> O <sub>2</sub>	I	Hypophosphites.
(Hyposulphite radical)—	SO <sub>2</sub> S	II	Thiosulphates.
Iodate radical—	IO <sub>3</sub>	I	Iodates.
Iodide radical—	I	I	Iodides.
Lactate radical—	C <sub>3</sub> H <sub>5</sub> O <sub>2</sub>	I	Lactates.
Lead+	Pb	II	Plumbic compounds.
Lithium+	Li	I	Lithium compounds.
Magnesium+	Mg	II	Magnesium compounds.
Manganous radical+	Mn	II	Manganous compounds.
Mercuric radical+	Hg	II	Mercuric compounds.
Mercurous radical+	Hg	I	Mercurous compounds.
Methyl+	CH <sub>3</sub>	I	Methyl compounds.
Nickelous radical+	Ni	II	Nickelous compounds.
Nitrate radical—	NO <sub>3</sub>	I	Nitrates.
Nitrite radical—	NO <sub>2</sub>	I	Nitrites.
Nitrogen—	N	III	Nitrides.
Oleate radical—	C <sub>18</sub> H <sub>33</sub> O <sub>2</sub>	I	Oleates.
Oxalate radical—	C <sub>2</sub> O <sub>4</sub>	II	Oxalates.
Oxygen—	O	II	Oxides, etc.
Permanganate radical—	MnO <sub>4</sub>	I	Permanganates.
Phenyl+	C <sub>6</sub> H <sub>5</sub>	I	Phenyl compounds.
Phenolsulphonate radical—	C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub>	I	Phenolsulphonates.
Phosphate radical—	PO <sub>4</sub>	III	Phosphates.
Phosphorus—	P	III	Phosphides.

<i>Name of Radical.</i>	<i>Symbol.</i>	<i>Number of Bonds.</i>	<i>Compounds Formed By It.</i>
Platinic radical+	Pt	IV	Platinic compounds.
Plumbic radical+	Pb	II	Plumbic compounds (lead).
Potassium+	K	I	Potassium compounds.
Pyroarsenate radical—	As <sub>2</sub> O <sub>7</sub>	IV	Pyroarsenates.
Pyroborate radical—	B <sub>2</sub> O <sub>7</sub>	II	Tetraborates.
Pyrophosphate radical—	P <sub>2</sub> O <sub>7</sub>	IV	Pyrophosphates.
Salicylate radical—	C <sub>7</sub> H <sub>5</sub> O <sub>2</sub>	I	Salicylates.
Silver+	Ag	I	Argentio compounds.
Sodium+	Na	I	Sodium compounds.
Strontium+	Sr	II	Strontium compounds.
Sulphate radical—	SO <sub>4</sub>	II	Sulphates.
Sulphide radical—	S	II	Sulphides.
Sulphite radical—	SO <sub>3</sub>	II	Sulphites.
(Sulphocarbonate)—	C <sub>6</sub> H <sub>5</sub> SO <sub>4</sub>	I	Phenolsulphonates.
Thiocyanate radical—	SCN	I	Thiocyanates (Sulphocyanates).
Tartrate radical—	C <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	II	Tartrates.
Tetraborate (or Pyroborate radical)	B <sub>4</sub> O <sub>7</sub>	II	Tetraborates (or Pyroborates).
Thiosulphate radical—	SO <sub>3</sub> S	II	Thiosulphates.
Valerate radical—	C <sub>6</sub> H <sub>5</sub> O <sub>2</sub>	I	Valerates.
Zinc+	Zn	II	Zinc compounds.

218. By consulting the foregoing table of radicals, the student may now write the customary molecular formulas of any of the common compounds formed by the radicals included in that table, observing the rule that the positive radical must be written first, and that the number of bonds furnished by one of the radicals must be the same as the number furnished by the other, so that the number of bonds furnished by each must accordingly be the least common multiple of the respective bonds or valence units of the single atoms or atomic groups of both. Thus—

To write potassium acetate, find potassium and note that it is a monad, or is univalent, or has but one bond; then find the acetate radical and observe that it, too, has but one bond; the formula for potassium acetate must, therefore, be  $\text{KC}_2\text{H}_3\text{O}_2$ .

To write sodium citrate observe that sodium has one bond and the citrate radical three bonds; it is, therefore, necessary to multiply Na by 3 in order to supply three bonds on the positive side to saturate the three negative bonds of the  $\text{C}_6\text{H}_5\text{O}_7$ ; hence the formula will be  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ .

To write the formula for normal calcium citrate note that Ca has two bonds and that  $\text{C}_6\text{H}_5\text{O}_7$  has three bonds; then, as twice three is 6 we must have 6 bonds on each side; to get six bonds from Ca it must be made  $\text{Ca}_3$  and to get six bonds from  $\text{C}_6\text{H}_5\text{O}_7$  it must be doubled; hence the formula will be  $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ .

To write aluminum oxide observe that Al has 3 bonds and O only 2; hence the formula must be  $\text{Al}_2\text{O}_3$ .

As Bi has three bonds and O two, the molecular formula for bismuth oxide must be  $\text{Bi}_2\text{O}_3$ .

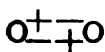
The formula for Rochelle salt or potassium-sodium tartrate must be  $\text{KNaC}_4\text{H}_4\text{O}_6$  because K and Na furnish one positive bond each to saturate the two negative bonds of the tartrate radical.

Ethyl benzoate must be  $\text{C}_2\text{H}_5\cdot\text{C}_7\text{H}_5\text{O}_2$  because ethyl ( $\text{C}_2\text{H}_5$ ) has one positive bond and the benzoate radical ( $\text{C}_7\text{H}_5\text{O}_2$ ) one negative bond.

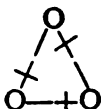
Ferric pyrophosphate must be  $\text{Fe}_4(\text{P}_2\text{O}_7)_3$  because the iron atoms of ferric compounds are trivalent while the pyrophosphate radical ( $\text{P}_2\text{O}_7$ ) is quadrivalent, and the least common multiple of 3 and 4 is 12, so that the positive radical, the ferric iron, must supply 12 bonds, and the negative radical, the pyrophosphate radical, also 12 bonds.

219. Representing the positive bonds or combining units by a plus sign or by a cross and the negative bonds by a minus sign or by a straight line we may indicate pictorially (but always only figuratively) how all the atoms in any molecule are tied together or directly and indirectly linked by bonds of opposite chemical polarity, respectively, as follows:

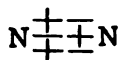
The hydrogen molecule may be represented by  $\text{H}+ - \text{H}$ ; the oxygen molecule by



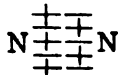
a molecule of ozone may be pictured as



a molecule of univalent nitrogen would be  $\text{N}+ - \text{N}$ , trivalent nitrogen



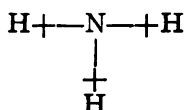
and one of quinquivalent nitrogen



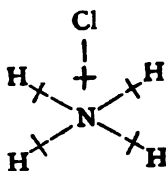
Hydrochloric acid may be pictured as  $\text{H}+\text{---}\text{Cl}$ .

The atomic linking of a molecule of water would be  $\text{H}+\text{---}\text{O}+\text{---}\text{H}$ , and that of hypochlorous acid  $\text{H}+\text{---}\text{O}+\text{---}\text{Cl}$ .

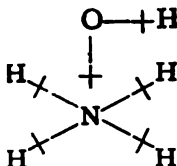
The atomic linking of the molecule of ammonia is shown by the figure



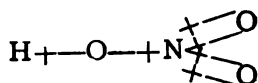
The atomic linking in the molecule of ammonium chloride is



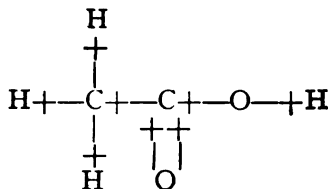
That of ammonium hydroxide is



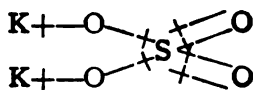
The atomic linking in a molecule of nitric acid is



A molecule of acetic acid may be pictured as



The atomic linking in potassium sulphate is



**220.** Whenever the bonds directly uniting any two atoms of any molecule are disconnected, the detached bonds must of course be potential positive bonds on the one side and an equal number of potential negative bonds on the other side.

If any open chain of radicals composing a molecule be severed at any point, it must thereby be divided into two free radicals, and the free (potential) terminal bond or bonds of one of these free radicals were positive, while the free (potential) terminal bond or bonds of the other free radical were necessarily negative when in actual combination. This is equivalent to stating that every molecule, unless it be a *closed* chain or a ring, no matter how many different radicals, elemental or compound, may be recognized as contained in it, can be arbitrarily divided into two radicals of which one was positive and the other negative in the original molecule. Thus the molecule of acetic acid containing the three distinct and well known compound radicals  $\text{CH}_3$  and  $\text{CO}$  and  $\text{OH}$ , which together form



can be divided into  $\text{H}$  and  $\text{O}.\text{OC}.\text{CH}_3$ , or into  $\text{HO}$  and  $\text{OC}.\text{CH}_3$ , or into  $\text{HO}.\text{OC}$  and  $\text{CH}_3$ , or even into  $\text{HO}.\text{OC}.\text{CH}_2$  and  $\text{H}$ .

But as the polarity of a free radical is but potential and not actual, and as it is determined by whatever other radical it enters into actual combination with, it follows that the polarity of a compound radical *may* be positive in one molecule but negative in another. Thus the polarity of  $\text{CH}_3$  is positive in  $\text{H}_3\text{CCl}$ , but negative in  $\text{HCH}_3$ .

A closed chain or ring can not be divided *at one point* into two separate radicals, but wherever the ring may be cut the free or potential combining units admit of the insertion or attachment of one or more additional radicals.

**221.** The correctness of the customary molecular formulas of inorganic compounds may *generally* be verified by the known valence of each of the component atoms or radicals; but as many elements have a variable valence the true molecular formula must frequently be determined by other means. But the sum of the positive bonds in actual combination in any molecule must be the same as the sum of the negative bonds in actual combination; there can be no free bond or bonds in any saturated molecule; and no molecular formula can be accepted as correct in which the atomic linking is inconsistent with the theories of valence and

polarity, or in which the atomic linking can not be traced in accordance therewith.

**222.** The molecular formulas of gaseous compounds may, according to modern chemical views, be verified or corrected with the aid of the hypotheses of Avogadro, Dulong and Petit, and Neumann and Regnault.

But the true molecular formulas of solids and liquids are not known with certainty.

Even the molecular formulas of volatile compounds can not be absolutely verified with reference to their vapor densities as it has been demonstrated that these may be twice as great at a lower temperature as at a higher one.

The molecular formula of ferric chloride deduced from its vapor density is assumed to be  $\text{FeCl}_3$  at temperatures above  $700^\circ$ , but  $\text{Fe}_2\text{Cl}_6$  at temperatures below that; the formula for ferric chloride in the liquid or solid condition can not be more simple than  $\text{Fe}_2\text{Cl}_6$ , and it is not impossible that it may be a multiple of it, but such a compound is a molecular and not an atomic combination.

**223.** Apparent inconsistencies and exceptions to rules must be encountered by all students of chemistry, and no good student can be content to set them aside until he is at least assured that they do not affect the results of actual work.

The apparently variable valence of elements; the fact that single atoms are apparently capable of continued existence in the free state; that two or more atoms may unite to form a more or less stable compound while still having one or more units of potential combining power unused; that compounds of the same elements in exactly the same proportions may not contain the same absolute number of atoms at all temperatures; that one and the same atom may have both positive and negative bonds in the same molecule; and that the molecular formulas and weights of some compounds as commonly represented and used may not be the true ones—all of these facts should be known and remembered by the student, but should not be permitted to disturb or confuse him because they do not affect the results of chemical analyses or of the methods employed for the preparation or manufacture of chemical products. Molecular formulas and weights are interdependent and correspondent, so that if a molecular formula is doubled the

molecular weight is also doubled, and if the weight is divided by two then the formula, also, must be cut in two.

Various combinations are known, which, although combinations in definite proportions, differ essentially from unquestioned chemical compounds. Chemical energy is so pervasive and transmutative in its effects that true chemical compounds generally exhibit radically different properties from those possessed by their component elements or by the substances from which they are produced, while combinations resulting from other forms of attraction generally retain several of the essential characteristics of at least one of the substances of which they consist, or possess properties strongly suggestive of their component molecules.

**True chemical compounds are inter-atomic systems; they are not inter-molecular combinations.**

Solutions are described by Mendeleeff as "fluid, unstable, definite chemical compounds *in a state of dissociation.*" But distinction is generally made between "physical solution" and "chemical solution," and it is agreed that in physical solution the identity and essential properties of the dissolved substance are preserved. The ratios of solubility generally differ at different temperatures. Yet solutions are not altogether mechanical mixtures for any two substances capable of forming solutions each with the other do not do so in all proportions.

That mercury forms certain amalgams in which that element enters into combination with other metals in definite proportions is not claimed; and amalgams are not chemical compounds because they exhibit essentially just such properties as might be expected of mere mixtures or of solutions.

The evidences of definite proportions in the composition of certain crystallizable alloys are unquestioned; yet alloys differ decidedly from chemical compounds for they are as strikingly metallic in all their properties as the individual metals of which they are composed.

The absorption of hydrogen by palladium, platinum, potassium, sodium and iron and the "occlusion" of hydrogen in some meteorites are admitted facts; it may also be admitted that combinations in apparently definite atomic proportions can be obtained containing hydrogen and potassium or sodium, etc. But these combinations are unstable, their recognition as chemical compounds must be regarded as violently inconsistent with the

well known ruling valence of the metals referred to and with deductions from the periodic law. Hence the so-called "~~hydrates~~ *hydrides*" of the metals, not differing from the amalgams and alloys in their essentially metallic properties, are radically unlike true chemical compounds.

Crystallized salts are known to contain water of crystallization in exact molecular proportions; but one molecule of the same salt may crystallize with either one molecule or with two molecules, or with some other number of molecules, of water, while all the chemical characteristics of the salt itself remain the same in all of these forms as well as in the anhydrous compound. Not even the crystalline form is *exclusively* dependent upon the chemical composition of the crystal, nor upon the proportion of its "water of crystallization," for it has been shown that copper sulphate crystallizes in monoclinic prisms (which is the form assumed by the crystals of ferrous sulphate) instead of in triclinic prisms (which is the normal form of copper sulphate crystals) whenever the copper salt crystallizes from a solution containing both ferrous sulphate and cupric sulphate and the proportion of iron salt present exceeds one molecule for every eight molecules of the copper compound; and crystals of cupric acetate may lose all of their water of crystallization without losing their crystalline form.

Isomorphous salts crystallize together, and their crystals may be readily made to grow in each other's solutions.

Solutions made of any given salt, whether the salt used contain no water or any number of molecules of water, are all identical if they contain the same proportion of the salt-radicals.

It is impossible to believe that the combinations described in the foregoing lines are produced directly by *atomic energy*; but it is quite evident that they result from some form or forms of *molecular energy*.

Other unstable molecular combinations or associations exist which are not understood and which can not be reconciled with accepted chemical theories. The crystalline body formed when a current of chlorine is conducted into very cold water and to which the composition  $\text{Cl}_2 \cdot 10\text{H}_2\text{O}$  has been assigned, is such a combination. The so-called "poly-iodides" of the alkali metals also belong to the class of *molecular combinations* more nearly

related to solutions, alloys, amalgams and hydrous or hydrated bodies than to true chemical compounds.

Two or more different kinds of molecules may be held to each other more or less firmly by *molecular attraction* to form molecular combinations in definite proportions, but no such combination can be called a chemical compound because chemical compounds are molecules formed by *atomic attraction* only, and there can therefore be but one continuous system of atomic linking in any true molecule.

**A true chemical compound consists of but one kind of molecules.**

That molecular combinations primarily depend upon the respective atomic compositions of the component molecules is undeniable; but no two different molecules can be *linked* together by their bonds, for they have no unoccupied bonds.

## CHAPTER XI.

### CHEMICAL NOMENCLATURE.

**224.** The systematic technical names of individual chemical compounds are necessarily compound names consisting of two or more words. These words are either the names of the elements or radicals entering into the compounds, or words derived from such names.

**225.** As the great majority of the inorganic chemical compounds are most conveniently, and properly, too, regarded as being composed of two radicals, one positive and the other negative, their systematic technical names generally consist of two words, the first of which is the name of its positive radical or a word derived from that, while the second word used in naming an inorganic chemical compound is one derived from or indicating the negative radical, or one which at once refers the compound to the class or group to which it belongs by reason of its composition and structure.

**226.** Thus the name of the compound which is formed when potassium unites with chlorine is "potassium chloride," because potassium is the positive radical of that compound, and the name chloride, derived from the name of the negative radical, is a generic title given to all compounds formed by any positive radical with chlorine.

The compound formed by lithium with bromine is, in accordance with the same system, called lithium bromide; a compound of silver and iodine is called silver iodide; one formed of calcium and fluorine is calcium fluoride; one composed of sodium and the compound radical cyanogen is called sodium cyanide; a compound of sulphur and oxygen is a sulphur oxide; one of carbon and sulphur is a carbon sulphide; one of chlorine and oxygen is a chlorine oxide; one of hydrogen and nitrogen is hydrogen nitride; one of zinc and phosphorus is zinc phosphide; one of calcium and carbon is called calcium carbide; a compound of barium with the compound radical hydroxyl,  $\text{HO}$ , is called barium hydroxide, and one of sodium and hydroxyl is sodium hydroxide.

A compound of lead with the nitrate radical,  $\text{NO}_3$ , is called lead nitrate; one composed of silver and the same nitrate radical is called silver nitrate; and the title calcium nitrate at once tells us that the substance so named is composed of calcium and  $\text{NO}_3$ .

The radical which is characteristic of all sulphates is  $\text{SO}_4$ ; therefore sodium sulphate must be composed of sodium and  $\text{SO}_4$ , and copper sulphate must be a compound of copper with  $\text{SO}_4$ .

Sodium nitrate is  $\text{NaNO}_3$ ; but sodium nitrite is  $\text{NaNO}_2$ , for  $\text{NO}_2$  is the negative radical of all nitrites.

**227.** The hydrogen acids are named after the respective halogens contained in them. Thus hydrochloric acid is the hydrogen acid of chlorine, or  $\text{HCl}$ ; hydrobromic acid is the hydrogen acid of bromine; and  $\text{HI}$  must be hydriodic acid.

Sulphuric acid must be a hydroxyl acid of sulphur; nitric acid must be a hydroxyl acid of nitrogen, and chloric acid must be composed of hydrogen, oxygen and chlorine, and thus also belong to the hydroxyl acids, for no hydrogen acid contains oxygen and all acids containing oxygen must be hydroxyl acids.

To distinguish between  $\text{HCl}$  and  $\text{HClO}_3$ , the  $\text{HCl}$  is called hydrochloric acid, while the  $\text{HClO}_3$  is called chloric acid; thus the prefix *hydro* in the name of an acid indicates that the acid named is a hydrogen acid and not a hydroxyl acid.

**228.** From the foregoing illustrations it is at once seen that in the construction of the technical names or titles of inorganic chemical compounds, the positive radical is indicated by a specific adjective, or by a specific substantive noun *used as an adjective*, while the negative radical is indicated by a generic substantive noun. Thus, in the title "potassium chloride," the word potassium is used as an adjective and specifies the particular kind of chloride, while the name chloride is the generic title given to all the members of a whole class of compounds.

Sometimes the positive radical is in fact indicated by a word in strictly adjective form, as when potassium chloride is called potassic chloride, silver nitrate is called argentic nitrate, and the oxide of calcium is called calcic oxide instead of calcium oxide.

**229.** In many cases it is necessary to use other and additional means by which the titles can be made sufficiently specific, and different adjectives derived from the same noun are frequently employed in such cases, as when the two different chlorides of

iron are distinguished from each other by naming one of them *ferrous* chloride and the other *ferric* chloride.

230. The following illustrations show how various needed technical terms are made up or coined from the names of the elements:

The name of the element nitrogen furnishes the substantive nouns nitrate, nitrite and nitride, and the adjectives nitric and nitrous.

The name chlorine furnishes the words chloride, chlorate, perchlorate, hypochlorite, chloric, chlorous, perchloric, and hypochlorous.

The terms sulphide, di-sulphide, tri-sulphide, penta-sulphide, sulphate, thiosulphate, sulphite, sulphuric and sulphurous are derived from the word sulphur.

Ferrous and ferric are adjectives derived from the Latin name of iron (*ferrum*), and the adjectives mercurous and mercuric are from the name mercury.

231. While certain characteristic *endings* are given to the technical terms constructed out of the names of the elements to indicate particular classes of compounds, certain *prefixes* are also employed for the purpose of making the necessary further distinctions. Such prefixes are employed in connection with both substantives and adjectives, with the names of the positive radicals as well as with the names indicating the negative radicals.

The necessity for both different endings and different prefixes will be recognized when it is remembered that five different compounds are formed by nitrogen and oxygen with each other; that there are four different oxides of chlorine, five (or seven) oxides of manganese, two of iron, two of mercury, etc.; there are two different sulphides of arsenic; hydrogen, phosphorus and oxygen form together five different kinds of acids; hydrogen, sulphur and oxygen form with each other three different acids represented by officinal salts.

The titles of so many different compounds formed by the same elements are rendered definitive and unambiguous by the combined use of significative endings and prefixes which are made parts of the names derived from the component elements or radicals, whether substantive or adjective, and often in the construction of but one single word.

Any element capable of exercising positive chemical polarity

with more than two different combining-values forms more than two series of compounds, or one distinct series for each of its several polarity-values (See also par. 232.)

**232.** The **endings** employed in the formation of *adjectives* are *-ic* and *-ous*, as in nitric and nitrous, sulphuric and sulphurous, carbonic and carbonous, arsenic and arsenous, cupric and cuprous, ferric and ferrous, mercuric and mercurous, etc.

The difference between an adjective with the ending *-ic* and an adjective ending in *-ous* is one of degree, only. Thus a *nitrous* compound contains a comparatively larger proportion of nitrogen than a *nitric* compound; an *antimonous* compound is more antimonial or contains more antimony than an *antimonic* compound; the adjectives *arsenical*, *arsenous* and *arsenic* all mean *containing arsenic*, but the word *arsenical* has no specific meaning as to degree, whereas an *arsenous* compound is one that contains more of the element called arsenic than an *arsenic* compound contains; a *ferrous* salt is richer in iron than the corresponding *ferric* salt; *mercurous* chloride contains more mercury than *mercuric* chloride; *cuprous* chloride contains more copper than *cupric* chloride; *sulphurous* acid has more sulphur in it than *sulphuric* acid; and *chlorous* oxide is richer in chlorine than *chloric* oxide.

Therefore, when any two compounds consist of the same two radicals, and the only difference between them as to composition lies in the different proportions, these two compounds may be easily distinguished from each other in their nomenclature by the use of the endings *-ic* and *-ous*, the name of the positive radical being turned into an adjective with the ending *-ic* to specify the compound containing the smaller proportion of the positive radical, and another adjective having the ending *-ous* to specify the compound containing a larger proportion of it.

The use of the endings *-ic* and *-ous* is commonly described as follows: When any given positive radical combines with any given negative radical in two different proportions, then the compound containing the greater proportion of the negative radical is called an *-ic* compound while the other is called an *-ous* compound. Thus, since mercury forms two compounds with oxygen, called oxides, the "higher oxide," which contains the greater proportion of oxygen, is called "mercuric oxide," while the other is called "mercurous oxide." In effect this form of statement amounts to the same as the other, for as mercurous oxide

contains relatively more mercury than the mercuric oxide it follows that mercurous oxide contains relatively less oxygen than the mercuric oxide. But, as the adjectives having the endings *-ous* and *-ic* are formed out of the names of the positive radical, the only correct and consistent explanation is one which takes due cognizance of the origin of the terms referred to. The English endings *-ic* and *-ous* are derived from the Latin endings *-icus* and *-osus*, respectively, which, in the construction of Latin adjectives, have the significance described.

Ferrous chloride is a "lower chloride" of iron than ferric chloride because the ferrous chloride contains a relatively greater proportion of iron (and hence less chlorine); and the ferric chloride is a "higher chloride" than the ferrous.

But the endings *-ic* and *-ous* when consistently employed in chemical nomenclature have a greater significance than that of merely distinguishing between lower and higher oxides, chlorides, etc., for each of these endings has reference to the molecular structures derived from a given polarity-value of the positive radical. To illustrate this fact we may mention that the term phosphoric always applies to compounds in which the element phosphorus has a polarity-value of +5, as in mono-meta-phosphoric (ortho-phosphoric) acid, di-meta-phosphoric ("meta-phosphoric") acid, tri-meta-di-phosphoric acid ("pyrophosphoric acid"), phosphoric anhydride, etc.; while a phosphorous compound is one containing phosphorus with a polarity-value of +3. A sulphuric compound contains sulphur with a polarity-value of +6, whether it be sulphuric anhydride, sulphuric acid, or thiosulphuric acid; but a sulphurous compound contains sulphur with a polarity-value of +4. A chloric compound contains chlorine with a polarity-value of +5, and a chlorous compound is one containing chlorine with a polarity-value of +3.

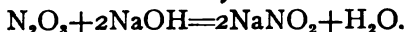
Whenever any element has more than two different positive polarity-values and accordingly forms more than two series of compounds, each series characterized by the particular polarity-value which that element exercises, then the endings *-ic* and *-ous* must be reinforced by the employment of prefixes as already indicated. Thus, since chlorine has four different positive polarity-values, namely +7, +5, +3 and +1, the compounds containing chlorine with a polarity-value of +7 are called *perchloric* compounds, those containing chlorine with a polarity-value of +5 are *chloric*,

those of chlorine with a polarity-value of  $+3$  are *chlorous*, and compounds containing chlorine with a polarity-value of  $+1$  are *hypochlorous* compounds.

While sulphuric compounds contain sulphur with a polarity-value of  $+6$  and *sulphurous* compounds are those of quadrivalent sulphur, the compounds formed by sulphur having a polarity-value of  $+2$  are *hyposulphurous* compounds, an example of which is sodium hyposulphite,  $\text{Na}_2\text{SO}_2$ . Sodium thiosulphate is a sulphuric compound because its acidic sulphur has a polarity-value of  $+6$  precisely as in ordinary sulphates.

Nitrogen, if it really forms all of the oxides and acids attributed to it, has a greater variety of polarity-values than any other element, namely  $+5$ ,  $+4$ ,  $+3$ ,  $+2$ ,  $+1$  and  $-3$ . But the nomenclature of the compounds formed by each of the five different kinds of positive nitrogen is much confused. Nitric acid contains quinquivalent nitrogen, nitrous acid contains trivalent nitrogen, and *hyponitrous* acid contains univalent nitrogen; but the names "nitric oxide" and "nitrous oxide" are misapplied, for the title of nitric oxide is commonly given to the compound  $\text{NO}$  in which the nitrogen has a polarity-value of  $+2$  instead of  $+5$ , and the title of nitrous oxide is given to the compound  $\text{N}_2\text{O}$  in which the nitrogen is a monad instead of a positive triad. The compound  $\text{N}_2\text{O}_5$  is really *the* nitric oxide, but to avoid the confusion caused by the misapplication of that title it is best to call it nitrogen pentoxide. The compound  $\text{NO}_2$  is well identified by the title nitrogen peroxide, and  $\text{N}_2\text{O}_4$  by that of nitrogen tetroxide. The compound  $\text{N}_2\text{O}_3$ , which is the only true nitrous oxide, must be called nitrogen trioxide to avoid confusion with  $\text{N}_2\text{O}$ , which has heretofore had that title. The compound  $\text{N}_2\text{O}_2$  might be called di-nitrogen di-oxide, and  $\text{NO}$  should be styled as mononitrogen mon-oxide, for the common title "nitric oxide" is erroneous and the name nitrogen dioxide can not be applied to  $\text{N}_2\text{O}_2$  because it might be misunderstood as meaning  $\text{NO}_2$ , nor can it be applied to  $\text{NO}$  since  $\text{NO}$  contains but one oxygen atom. The compound  $\text{N}_2\text{O}$  is hyponitrous oxide, and not nitrous oxide, for hyponitrous acid,  $\text{HNO}$ , breaks down into  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$  and the nitrogen has the polarity-value of  $+1$  in both the  $\text{N}_2\text{O}$  and the  $\text{HNO}$ . Nitrogen trioxide is the oxide corresponding to nitrous acid, for the nitrogen in both compounds has the polarity-value

+3 and sodium nitrite is formed when  $\text{N}_2\text{O}_3$  is passed into a solution of sodium hydroxide:



Yet, unfortunately, it is the custom to call  $\text{N}_2\text{O}$  nitrous oxide, although  $\text{HNO}$  is correctly called hyponitrous acid, and to call  $\text{NO}$  nitric oxide, although it does not correspond to nitric acid, while nitrous acid,  $\text{HNO}_2$ , and nitric acid,  $\text{HNO}_3$ , are both correctly named.

*Hypophosphorous* acid,  $\text{HPH}_2\text{O}_2$ , is correctly named because the phosphorus in that molecule has a polarity-value of +1.

Boric acid is  $\text{H}_3\text{BO}_3$ ; but borax is also a boric compound because the boron in  $\text{Na}_2\text{B}_4\text{O}_7$  has the same polarity-value as the boron in  $\text{H}_3\text{BO}_3$  and the kind of boric acid corresponding to  $\text{Na}_2\text{B}_4\text{O}_7$  is penta-meta-tetra-boric acid, or a boric acid formed by the splitting off of five molecules of water from four molecules of normal boric acid.

**233.** The principal endings employed in the formation of *substantive* nouns to be used as class titles of inorganic chemical compounds are *-ide*, *-ate* and *-ite*.

The technical names possessing these endings are derived from the names of the negative radicals of the compounds named. Thus nearly all compounds containing only two elements have generic names ending with *-ide*.

Accordingly we have  $\text{PbO}$ =lead oxide;  $\text{PbS}$ =lead sulphide;  $\text{PbCl}_2$ =lead chloride;  $\text{PbI}_2$ =lead iodide;  $\text{KBr}$ =potassium bromide;  $\text{Hg}(\text{CN})_2$ =mercuric cyanide;  $\text{H}_3\text{N}$ =hydrogen nitride (ammonia),  $\text{CaF}_2$ =calcium fluoride;  $\text{Ca}_2\text{C}$ =calcium carbide.

The ending *-ate* is given to the names of salts formed by “-ic acids,” and the ending *-ite* is given to the names of salts formed by “-ous acids.”

An -ic acid being one that contains a relatively larger proportion of oxygen than the corresponding -ous acid, we can readily understand the meaning of the nouns having the endings *-ate* and *-ite*, respectively.

Sulphuric acid contains relatively less sulphur and relatively more oxygen than sulphurous acid does, and the salts formed by sulphuric acid are called sulphates.

Sulphurous acid, which contains a relatively greater proportion of sulphur and accordingly a relatively less proportion of oxygen than sulphuric acid contains, forms salts which are called sul-

phites. Hence a sulphate contains more oxygen or less sulphur than the sulphite of the same positive radical.

Nitrous acid forms salts called nitrites, but the salts of nitric acid are called nitrates.

Chloric acid forms salts called chlorates; but hypochlorous acid forms salts called hypochlorites.

Phosphoric acid forms phosphates; but hypophosphorous acid forms hypophosphites.

Carbonates are the salts formed by carbonic acid, silicates are the salts of silicic acid, arsenates the salts of arsenic acid, arsenites the salts of arsenous acid, etc.

**234.** The principal **prefixes** employed in forming the technical terms of chemical nomenclature are the following:

*1. Derived from Greek numerals—*

*Mono-* or *Mon-*, meaning one or single.

*Di-* (or *Dis-*), meaning two or twice.

*Tri-* (or *Tris-*), meaning three or thrice.

*Tetra-*, meaning four.

*Penta-*, meaning five.

*Hexa-*, meaning six.

*Hepta-*, meaning seven.

*Octo-*, meaning eight.

*2. Prefixes derived from Latin numerals—*

*Un-* or *Uni-*, meaning one or single.

*Duo-* or *Bi-* or *Bin-* or *Bis-*, meaning two or twice.

*Ter-* or *Tri-*, meaning three or thrice.

*Quadri-* or *Quadra-*, meaning four.

*Quinque* or *Quinqui-*, meaning five.

*Sexa-* or *Sexi-*, meaning six.

*Septi-* or *Sept-*, meaning seven.

*Octo-* or *Octi-*, meaning eight.

*3. Other prefixes—*

*Super-* (obsolete except in pharmacy), meaning above, higher, over, in excess.

*Hyper-* (obsolete), meaning above, higher, over, in excess.

*Per-*, meaning thorough, through, to the full extent.

*Sesqui-* (obsolete except in pharmacy), meaning half as much more, or once and a half.

*Deuto-* or *Deut-* (obsolete), meaning twice, or two.

*Sub-*, meaning under, lower or below.

*Hypo-*, meaning under, lower or below.

*Proto-* or *Prot-* (now obsolete), meaning first or lower.

*Ortho-*, meaning straight, regular, common, usual, original.

*Meta-*, meaning beyond, after, abnormal, altered, or different.

*Para-*, meaning changed, different, altered, beside, beyond.

*Pyro-*, meaning as produced by fire or high heat.

*Thio-*, (from *theion*, sulphur) means containing sulphur.

The following illustrations will suffice to render clear the employment and meaning of these prefixes:

A monoxide is an oxide containing but one oxygen atom.

A dioxide is an oxide containing two oxygen atoms.

A trichloride is a chloride containing three chlorine atoms.

A trisnitrate is a nitrate in which the nitrate-radical is trebled or contained three times in each molecule.

A tetrabromide is a bromide containing four bromine atoms.

A pentachloride contains five chlorine atoms.

A pentoxide contains five oxygen atoms.

A metallic bicarbonate is one containing twice as much of the carbonate-radical in proportion to the metal as is contained in the normal carbonate.

A tersulphate is a sulphate in which the sulphate radical is trebled.

Permanganic acid contains more oxygen than manganic acid contains.

Sesquichloride of iron contains one and one-half times as much chlorine as the lower chloride of iron contains.

A deutoxide contains twice as much oxygen as the lower oxide.

A biniodide contains twice as much iodine as the lower iodide.

A subchloride is a lower chloride.

Hypochlorous oxide is a lower oxide of chlorine than chlorous oxide is.

Protochloride of iron is the first or lower chloride of iron.

Orthophosphoric acid is the ordinary or common phosphoric acid.

Metaphosphoric acid is different from the ordinary acid.

Pyrophosphoric acid is the acid produced by strongly heating the ortho-phosphoric acid.

A thiosulphate is a sulphate containing more sulphur than is contained in the corresponding sulphate.

A superoxide is a higher oxide.

Perchloride of iron is a chloride of iron containing the greatest proportion of chlorine with which iron can combine.

Persulphate of iron is a sulphate of iron containing the greatest possible proportion of the sulphate radical.

But a *peroxide* is an oxide performing neither basic nor acidic functions and having usually the formula  $RO_2$ .

**235.** Binary compounds (compounds formed of but two kinds of atoms) can be named with great preciseness by the use of numeral prefixes for both words composing their technical titles, the prefixes being used to indicate the number of atoms. Thus—

$N_2O$  could be called dinitrogen monoxide.

$NO$  could be called mononitrogen monoxide.

$NO_2$  could be called mononitrogen dioxide.

$N_2O_3$  could be called dinitrogen trioxide.

$N_2O_4$  could be called dinitrogen tetroxide.

$N_2O_5$  could be called dinitrogen pentoxide.

In other cases where the number of atoms of the positive elemental radical does not vary in the several compounds it forms with any given negative radical, the prefix can be (and very frequently *is*) used only with the second word in the title. Thus we say carbon monoxide for  $CO$ , and  $CO_2$  is called carbon dioxide.

**236.** There are several sets of titles or names by which chemical compounds are designated in pharmacy and medicine.

Some of these titles are scientific and *systematic* chemical terms which indicate the chemical composition of the substances named. The title "potassium chloride" is such a title because it names the component elements and defines the structure of the compound. The titles mercurous chloride, ferric chloride, aluminum hydroxide, magnesium sulphate and silver nitrate are also systematic titles.

But such titles as calomel, alum, borax, ammonia, corrosive sublimate, cream of tartar, tartar emetic, lime, chalk, etc., are wholly *arbitrary*. They are not in accordance with any system, and convey no information as to the chemical character of the substances named.

It is further to be remembered that physicians and pharmacists use two parallel sets of titles, one set of titles (usually technical) which are *latinic* in their form, and another set of titles in the language of the country using them. The *non-latinic* titles may be *technical* or *not technical*.

The pharmacopœias of the world contain both latinic and non-latinic titles, and preference is universally given to the latinic titles. Hence the student must learn the official latinic and non-latinic titles as well as the *systematic* titles.

The official titles are, in several instances, not only unsystematic and unscientific from the standpoint of chemistry, but they are sometimes altogether false, having been retained long after their meaning had become essentially changed. Thus the title arsenous acid given by the pharmacopœias to arsenous oxide,  $\text{As}_2\text{O}_3$  (or  $\text{As}_4\text{O}_6$ ) was at one time in accord with the views of chemists, but is not in harmony with the chemistry of to-day.

The official nomenclature of chemical compounds has not kept pace with the advance of the science, and students must, therefore, be careful not to be misled by the few wholly erroneous titles still employed by the pharmacopœias, such as the titles: "arsenous acid" (which should be arsenous oxide), "carbolic acid" (which should be phenol), "chromic acid" (which should be chromic anhydride), "aluminum hydrate" (which should be aluminum hydroxide), "ferric hydrate" (which should be ferric hydroxide), "solution of lime" (which should be solution of calcium hydroxide), "potassium bichromate" (which should be potassium dichromate, because the title bichromate usually conveys the idea that the compound is an acid salt, which is not true, whereas the title dichromate simply indicates that it is a salt having two chromium atoms in its molecule, which is true), "sodium borate" (which should be sodium tetraborate, or, perhaps, pyroborate), "sodium hyposulphite" (which should be sodium thiosulphate), and "sodium sulphocarbolate" (which should be sodium phenosulphonate, or, still better, sodium parphenolsulphonate).

The unsystematic titles alumen, calx, ammonia, magnesia, potassa and soda are less objectionable because they do not convey false conceptions.

**237.** Since the titles of the inorganic chemical compounds, whether latinic or non-latinic, are derived, as a rule, from the

names of the elements, it is necessary that the student shall know these names well. And in order to learn to use correctly the latinic titles of compounds he must first know the latinic names of the elements with their genitives.

The following table contains the names of all elements entering into chemical compounds employed in medicine and pharmacy:

ENGLISH NAME.	LATINIC NAME.	
	<i>Nominative.</i>	<i>Genitive.</i>
Aluminum.	Alu'minum.	Alu'mini.
Antimony.	Antimo'num.	Antimo'ni.
Do.	Sti'bium.	Sti'bii.
Arsenic.	Arse'num.	Arse'ni.
Barium.	Ba'rium.	Ba'rii.
Bismuth.	Bismu'thum.	Bismu'thi.
Boron.	Bo'rum.	Bo'ri.
Bromine.	Bro'mum.	Bro'mi.
Cadmium.	Cad'mium.	Cad'mii.
Calcium.	Cal'cium.	Cal'cii.
Carbon.	Carbo'neum.	Carbo'nei.
Cerium.	Ce'rium.	Ce'rii.
Chlorine.	Chlo'rum.	Chlo'ri.
Chromium.	Chro'mium.	Chro'mii.
Copper.	Cu'prum.	Cu'pri.
Gold.	A'urum.	A'uri.
Hydrogen.	Hydroge'nium.	Hydroge'nii.
Iodine.	Iod'um.	Iod'i.
Iron.	Fer'rum.	Fer'ri.
Lead.	Plum'bum.	Plum'bi.
Lithium.	Li'thium.	Li'thii.
Magnesium.	Magne'sium.	Magne'sii.
Manganese.	Manga'num.	Manga'ni.
Mercury.	Hydrar'gyrum.	Hydrar'gyri.
Do.	Mercu'rium.	Mercu'rii.
Nitrogen.	Nitroge'nium.	Nitroge'nii.
Oxygen.	Oxyge'nium.	Oxyge'nii.
Phosphorus.	Phos'phorus.	Phos'phori.
Potassium.	Potas'sium.	Potas'sii.
Do.	Ka'lium.	Ka'lii.
Silicon.	Sili'cium.	Sili'cii.
Silver.	Argen'tum.	Argen'ti.
Sodium.	So'dium.	So'dii.
Do.	Na'trium.	Na'trii.
Strontium.	Stron'tium.	Stron'tii.
Sulphur.	Sul'phur.	Sul'phuris.
Tin.	Stan'num.	Stan'ni.
Zinc.	Zin'cum.	Zin'ci.

Accentuation marks are placed *after* the syllables upon which the accent rests in the pronunciation of the latinic names.

Three of the elements have two names each. The titles potassium, sodium and antimonum are used in all English speaking countries; the titles kalium, natrium and stibium are employed in German speaking countries and elsewhere.

All the latinic titles of the elements have the ending *-um* or *-ium* in the nominative and *-i* or *-ii* in the genitive *with two exceptions only*. These exceptions are phosphorus, genitive phosphori; and sulphur, genitive sulphuris.

Phosphorus is masculine; all the other latinic titles of the elements are neuter.

**238.** The generic titles employed in naming classes of inorganic chemical compounds are the following:

ENGLISH TITLES.	LATINIC TITLES.	
	<i>Nominative.</i>	<i>Genitive.</i>
Acid.	A'cidum.	A'cidi.
Anhydride.	Anhy'dridum.	Anhy'dridi.
Bromide.	Bro'midum.	Bro'midi.
Chloride.	Chlo'ridum.	Chlo'ridi.
Cyanide.	Cya'nidum.	Cya'nidi.
Ferricyanide.	Ferricya'nidum.	Ferricya'nidi.
Ferrocyanide.	Ferrocya'nidum.	Ferrocya'nidi.
Hydrobromide.	Hydrobro'midum.	Hydrobro'midi.
Hydrochloride.	Hydrochlo'ridum.	Hydrochlo'ridi.
Hydriodide.	Hydrojod'idum.	Hydrojod'idi.
Hydroxide.	Hydrox'idum.	Hydrox'idi.
Iodide.	Iod'idum.	Iod'idi.
Oxide.	Ox'idum.	Ox'idi.
Phosphide.	Phos'phidum.	Phos'phidi.
Sulphide.	Sul'phidum.	Sul'phidi.

All of the foregoing latinic titles are neuter and follow the second declension.

Acetate.	Ace'tas.	Aceta'tis.
Arsenate.	Arse'nas.	Arsena'tis.
Arsenite.	Arse'nis.	Arseni'tis.
Benzoate.	Ben'zoas.	Benzoa'tis.
Bicarbonate.	Bicarbo'nas.	Bicarbona'tis.
Bichromate.	Bichro'mas.	Bichroma'tis.
Bisulphate.	Bisul'phas.	Bisulpha'tis.
Bisulphite.	Bisul'phis.	Bisulphi'tis.
Bitartrate.	Bitar'tras.	Bitartra'tis.
Carbonate.	Carbo'nas.	Carbona'tis.
Chlorate.	Chlo'ras.	Chlora'tis.
Citrate.	Ci'tras.	Citra'tis.
Dichromate.	Dichro'mas.	Dichroma'tis.
Hydrate.	Hy'dras.	Hydra'tis.
Hydrobromate.	Hydrobro'mas.	Hydrobroma'tis.
Hydrochlorate.	Hydrochlo'ras.	Hydrochlora'tis.
Hydriodate.	Hydrojod'as.	Hydrojoda'tis.
Hypophosphite.	Hypophos'phis.	Hypophosphi'tis.
Hyposulphite.	Hyposul'phis.	Hyposulphi'tis.
Iodate.	Iod'as.	Ioda'tis.
Lactate.	Lac'tas.	Lacta'tis.
Lactophosphate.	Lactophos'phas.	Lactophospha'tis.
Nitrate.	Ni'tras.	Nitra'tis.
Nitrite.	Ni'tris.	Nitri'tis.

Oleate.	O'leas.	Olea'tis.
Oxalate.	Ox'alas.	Oxala'tis.
Permanganate.	Permanga'nas.	Permangana'tis.
Phenolsulphonate.	Phenolsulpho'nas.	Phenosulphona'tis.
Phosphate.	Phos'phas.	Phospha'tis.
Pyrophosphate.	Pyrophos'phas.	Pyrophospha'tis.
Salicylate.	Salicy'las.	Salicyla'tis.
Silicate.	Si'licas.	Silica'tis.
Subacetate.	Subace'tas.	Subaceta'tis.
Subcarbonate.	Subcarbo'nas.	Subcarbona'tis.
Subnitrate.	Subni'tras.	Subnitra'tis.
Subsulphate.	Subsul'phas.	Subsulpha'tis.
Sulphate.	Sul'phas.	Sulpha'tis.
Sulphite.	Sul'phis.	Sulphi'tis.
Sulphocarbonate.	Sulphocarbo'las.	Sulphocarbola'tis.
Tannate.	Tan'nas.	Tanna'tis.
Tartrate.	Tar'tras.	Tartra'tis.
Tersulphate.	Tersul'phas.	Tersulpha'tis.
Thiosulphate.	Thiosul'phas.	Thiosulpha'tis.

All the latinic titles ending in *-as* or in *-is* are masculine; those ending in *-as* in the nominative have the genitive ending *-atis*, and those ending in *-is* in the nominative have the genitive ending *-itis*.

239. Examples of the latinic adjectives used in connection with the titles of inorganic chemical compounds are as follows:

## ENGLISH ADJECTIVES.

## LATINIC ADJECTIVES.

	<i>Masculine.</i>	<i>Feminine.</i>	<i>Neuter.</i>
Acetic.	Ace'ticus.	Ace'tica.	Ace'ticum.
Antimonous.	Antimono'sus.	Antimono'sa.	Antimono'sum.
Arsenous.	Arseno'sus.	Arseno'sa.	Arseno'sum.
Arsen'ic.	Arse'nicus.	Arse'nica.	Arse'nicum.
Benzoic.	Benzo'icus.	Benzo'ica.	Benzo'icum.
Bismuthous.	Bismutho'sus.	Bismutho'sa.	Bismutho'sum.
Boric.	Bo'ricus.	Bo'rica.	Bo'ricum.
Carbolic.	Carbo'licus.	Carbo'lica.	Carbo'licum.
Carbonic.	Carbo'nicus.	Carbo'nica.	Carbo'nicum.
Chlorinated.	Chlorina'tus.	Chlorina'ta.	Chlorina'tum.
Chromic.	Chro'micus.	Chro'mica.	Chro'micum.
Citrated.	Citra'tus.	Citra'ta.	Citra'tum.
Citric.	Ci'tricus.	Ci'trica.	Ci'tricum.
Ferric.	Fer'ricus.	Fer'rica.	Fer'ricum.
Ferrous.	Ferro'sus.	Ferro'sa.	Ferro'sum.
Hydrated.	Hydra'tus.	Hydra'ta.	Hydra'tum.
Hydriodic.	Hydrojod'icus.	Hydrojod'ica.	Hydrojod'icum.
Hydrobromic.	Hydrobro'micus.	Hydrobro'mica.	Hydrobro'micum.
Hydrochloric.	Hydrochlo'ricus.	Hydrochlo'rica.	Hydrochlo'ricum.
Hydrocyanic.	Hydrocy'a'nicus.	Hydrocy'a'nica.	Hydrocy'a'nicum.
Hypophosphorous.	Hypophosphoro'-sus.	Hypophosphoro'-sa.	Hypophosphoro'-sum.
Mercuric.	Mercu'ricus.	Mercu'rica.	Mercu'ricum.
Do.	Hydrargy'ricus.	Hydrargy'rica.	Hydrargy'ricum.
Mercurous.	Mercuro'sus.	Mercuro'sa.	Mercuro'sum.
Do.	Hydrargyro'sus.	Hydrargyro'sa.	Hydrargyro'sum.
Oleic.	Ole'icus.	Ole'ica.	Ole'icum.
Oxalic.	Oxa'licus.	Oxa'lica.	Oxa'licum.
Phosphoric.	Phospho'ricus.	Phospho'rica.	Phospho'ricum.

## ENGLISH ADJECTIVES.

	<i>Masculine.</i>
Salicylic.	Salicy'licus.
Sulphurated.	Sulphura'tus.
Sulphuric.	Sulphu'ricus.
Sulphurous.	Sulphuro'sus.
Tartaric.	Tarta'ricus.
Valerianic.	Valeria'nicus.
Do, or Valeric.	Vale'ricus.

## LATINIC ADJECTIVES.

<i>Feminine.</i>	<i>Neuter.</i>
Salicy'lica.	Salicy'licum.
Sulphura'ta.	Sulphura'tum.
Sulphu'rica.	Sulphu'ricum.
Sulphuro'sa.	Sulphuro'sum.
Tarta'rica.	Tarta'ricum.
Valeria'nica.	Valeria'nicum.
Vale'rica.	Vale'ricum.

**240.** The names of acids consist of adjectives specifying their kind and the word acid or acidum. In the English titles of the acids the adjective is placed first, while in the latinic titles the order is reversed. The adjective in each case is, of course, so far as possible, derived from the name of the acidic element and in cases where the same element forms more than one hydroxyl acid the ending of the adjective determines its kind, or a prefix is employed wherever necessary.

The following are the most common acids represented by pharmaceutical chemicals:

## ENGLISH TITLES.

Acetic Acid.  
 Arsenous Acid.  
 Benzoic Acid.  
 Boric Acid.  
 Carbonic Acid.  
 Chromic Acid.  
 Citric Acid.  
 Gallic Acid.  
 Hydriodic Acid.  
 Hydrobromic Acid, Diluted.  
 Hydrochloric Acid.  
 Diluted Hydrochloric Acid.  
 Hydrocyanic Acid.  
 Hypochlorous Acid.  
 Hypophosphorous Acid.  
 Lactic Acid.  
 Metaphosphoric Acid.  
 Nitric Acid.  
 Nitrous Acid.  
 Oleic Acid.  
 Oxalic Acid.  
 Phosphoric Acid.  
 Diluted Phosphoric Acid.  
 Glacial Phosphoric Acid.  
 Salicylic Acid.  
 Silicic Acid.  
 Stearic Acid.  
 Sulphuric Acid.  
 Diluted Sulphuric Acid.  
 Sulphurous Acid.  
 Tannic Acid.  
 Tartaric Acid.  
 (Valeric Acid, or)  
 Valerianic Acid.

## LATINIC TITLES.

A'cidum Ace'ticum.  
 A'cidum Arseno'sum.  
 A'cidum Benzo'icum.  
 A'cidum Bo'ricum.  
 A'cidum Carbo'nicum.  
 A'cidum Chro'micum.  
 A'cidum Ci'tricum.  
 A'cidum Gal'licum.  
 A'cidum Hydrojod'icum.  
 A'cidum Hydrobro'micum.  
 A'cidum Hydrochlo'ricum.  
 A'cidum Hydrochlo'ricum Dilu'tum.  
 A'cidum Hydrocy'a'nicum.  
 A'cidum Hypochloro'sum.  
 A'cidum Hypophosphoro'sum.  
 A'cidum Lac'ticum.  
 A'cidum Metaphospho'ricum.  
 A'cidum Ni'tricum.  
 A'cidum Nitro'sum.  
 A'cidum Ole'icum.  
 A'cidum Oxa'licum.  
 A'cidum Phospho'ricum.  
 A'cidum Phospho'ricum Dilu'tum.  
 A'cidum Phospho'ricum Glacia'le.  
 A'cidum Salicy'licum.  
 A'cidum Sili'cium.  
 A'cidum Stea'ricum.  
 A'cidum Sulphu'ricum.  
 A'cidum Sulphu'ricum Dilu'tum.  
 A'cidum Sulphuro'sum.  
 A'cidum Tan'nicum.  
 A'cidum Tarta'ricum.  
 (A'cidum Vale'ricum, or)  
 A'cidum Valeria'nicum.

**241.** Illustrations of compound titles made up of the words already mentioned in this chapter, and in accordance with the general rules stated, are contained in the following list, which also shows some examples of titles of pharmaceutical preparations containing inorganic chemical compounds:

ENGLISH TITLES.	LATINIC TITLES.
Aluminum Hydrate, or Aluminum Hydroxide.	Alu'mini Hy'dras, or Alu'mini Hydrox'idum.
Antimony Oxide.	Antimo'ni Ox'idum.
Arsenic Iodide.	Arse'ni Iod'idum.
Arsenic Iodide.	Arse'nicum Iod'idum, or Iod'idum Arse'nicum.
Bismuth Subnitrate.	Bismu'thi Subni'tras.
Calcium Chloride.	Cal'cii Chlo'ridum.
Cerium Oxalate.	Ce'rii Ox'alas.
Chlorine Water.	A'qua Chlo'ri.
Copper Sulphate, or Cupric Sulphate.	Cu'pri Sul'phas, or Cu'pricus Sulphas, or Sul'phas Cu'pricus.
Gold Chloride, or Auric Chloride.	A'uri Chlo'ridum, or Au'ricum Chlo'ridum, or Chlo'ridum Au'ricum.
Hydrogen Dioxide.	Hydroge'nii Diox'idum.
Solution of Hydrogen Dioxide.	Solu'tio Hydroge'nii Diox'idi, or Li'quor Hydroge'nii Diox'idi, or A'qua Hydroge'nii Diox'idi.
Tincture of Iodine.	Tinctu'ra Io'di.
Compound Solution of Iodine.	Li'quor Iodi Compo'situs.
Reduced Iron.	Fer'rum Reduc'tum.
Powdered Iron.	Fer'rum Pulvera'tum.
Sulphate of Iron.	Fer'ri Sul'phas.
Ferrous Sulphate.	Ferro'sus Sul'phas, or Sul'phas Ferro'sus.
Dried Ferrous Sulphate.	Fer'ri Sul'phas Exsicca'tus, or Ferro'sus Sul'phas Exsicca'tus.
Turbidated Alum.	Alu'men Turbida'tum.
Ferric Hydroxide.	Fer'ricum Hydrox'idum.
Chloride of Iron.	Fer'ri Chlo'ridum.
Ferrous Chloride.	Ferro'sum Cho'ridum.
Ferric Chloride.	Fer'ricum Chlo'ridum.
Ferroso-ferric Oxide.	Ferro'so-fer'ricum Ox'idum.
Ferrous Iodide.	Ferro'sum Iod'idum.
Syrup of Ferrous Iodide.	Syru'pus Ferro'si Iod'idi.
Iodide of Iron.	Fer'ri Iod'idum.
Syrup of Iodide of Iron.	Syru'pus Fer'ri Iod'idi.
Saccharated Iodide of Iron.	Fer'ri Iod'idum Sacchara'tum.
Lead Iodide, or Plumbic Iodide.	Plum'bi Iod'idum, or Plum'bicum Iodidum.
Manganous Sulphate.	Mangano'sus Sul'phas.
Sulphate of Manganese.	Manga'ni Sulphas.
Oxide of Mercury.	Hydrar'gyri Ox'idum, or Mercur'ii Ox'idum.
Mercurous Oxide.	Hydrargyro'sum Ox'idum, or Mercurio'sum Ox'idum.
Mercuric Oxide.	Hydrargy'ricum Ox'idum, or Mercur'icum Ox'idum.

## ENGLISH TITLES.

Mercurous Iodide.

Mercuric Iodide.

Mild Chloride of Mercury.

Mild Mercurous Chloride.

Silver Nitrate, or

Argentie Nitrate.

Nitrate of Silver.

Strontium Bromide.

Bromide of Strontium.

Iodide of Sulphur.

Sulphuric Iodide.

Potassium Ferrocyanide.

Sodium Acetate.

Solution of Potassium Arsenite.

Sodium Bicarbonate.

Soluble Ferric Phosphate.

Soluble Phosphate of Iron.

Solution of Subacetate of Lead.

Solution of Arsenous Acid.

Precipitated Sulphur.

Crystallized Phenol.

Sublimed Calomel.

## LATINIC TITLES.

Mercuro'sum Iod'idum, or

Hydrargyro'sum Iod'idum.

Hydrargy'ricum Iod'idum, or

Mercu'ricum Iod'idum.

Hydrar'gyri Chlo'ridum Mi'te.

Hydrargyro'sum Chlo'ridum Mi'te,

or

Mercuro'sum Chlo'ridum Mite.

Argen'ticus Ni'tras.

Argen'ti Nitras.

Stron'ticum Bro'midum.

Stron'tii Bro'midum.

Sul'phuris Iod'idum.

Sulphu'ricum Iod'idum.

Potas'sii Ferrocya'nidum.

So'dii Ace'tas.

Li'quor Potas'sii Arseni'tis.

So'dii Bicarbo'nas.

Fer'ricus Phos'phas Solu'bilis.

Fer'ri Phos'phas Solu'bilis.

Li'quor Plum'bi Subaceta'tis.

Li'quor A'cidi Arseno'si.

Sul'phur Præcipita'tum.

Phe'nol Crystallisa'tum.

Cal'omel Sublima'tum.

## CHAPTER XII.

### CLASSIFICATION OF INORGANIC CHEMICAL COMPOUNDS—BINARY COMPOUNDS.

**242.** Armed with a knowledge of the atomic hypothesis, of the differences between atoms and molecules, of chemical polarity and valence, and of chemical notation and nomenclature, the student may now not only build compound molecules on paper, but he may begin to intelligently classify these molecules. This theoretical study is as necessary as laboratory work in the acquisition of a practical knowledge of chemistry.

Our building materials will be the elements represented by their respective symbols. We shall fit them together on paper according to their polarities and valences, and we shall arrange the molecular formulas thus theoretically constructed into classes according to their similarities or analogies of structure, which can be easily done without any knowledge of the properties or appearance of the compounds represented by the formulas we thus write, but which can not be done at all without the aid of a system of graphic representation, even if we may be quite familiar with the individual kinds of matter which our purely theoretical symbolic formulas stand for.

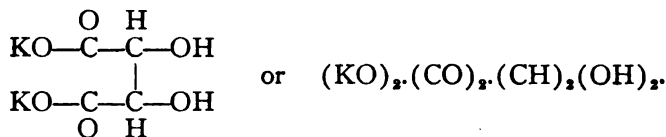
And as we thus learn the structure of the most important tribes of inorganic compounds we shall also discuss some of their tribal and family traits and some of their offspring.

**243.** Compound molecules may consist of but two elements, or of several. They may consist of two or more radicals. The radicals composing the molecules may be elemental, or compound, or both.

Inorganic chemical compounds are most conveniently studied and classified with the aid of the conception that each molecule usually consists of two radicals, one positive and the other negative. That is, in effect, the universally adopted plan, whether explicitly taught or not. Thus the metallic oxygen salts and the hydroxyl acids are represented as respectively composed of the metal and the acid-residue, and of hydrogen and the acid-residue,

or of two compound radicals. The molecule of sulphuric acid is represented as composed of H and  $\text{SO}_4$ , calcium sulphate as composed of Ca and  $\text{SO}_4$ , phosphoric acid of H and  $\text{PO}_4$ , ammonium phosphate of  $\text{H}_4\text{N}$  and  $\text{PO}_4$ , ammonium hypophosphite of  $\text{H}_4\text{N}$  and  $\text{PH}_2\text{O}_2$ , and ammonium acetate of  $\text{H}_4\text{N}$  and  $\text{C}_2\text{H}_3\text{O}_2$  or of  $\text{H}_4\text{N}$  and  $\text{OCOCH}_3$ . Or sulphuric acid is represented as composed of HO and  $\text{SO}_2$ , calcium sulphate of  $\text{CaO}_2$  and  $\text{SO}_2$ , and ammonium acetate of  $\text{H}_4\text{NO}$  and  $\text{COCH}_3$ .

More than two radicals enter into the formation of "double salts," as in  $\text{KNaC}_4\text{H}_4\text{O}_6$ ; acid salts, as in  $\text{KHSO}_4$ , and many other compounds. But the general structure of most of these compounds which constitute exceptions to the rule laid down can not be said to deviate essentially from it. At the same time, while we represent potassium tartrate as  $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$  and as composed of the positive or basic element K and the negative compound radical or acid-residue  $\text{C}_4\text{H}_4\text{O}_6$ , we are not to forget that  $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$  is probably



which we can simplify into  $\text{K}_2\text{O}_2(\text{CO})_2(\text{CH})_2(\text{OH})_2$ , or into  $\text{K}_2\text{O}_2\text{C}_4\text{H}_4\text{O}_6$ , and into  $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ , which is not a *structural* formula, but a convenient condensed expression. All tartrates may be written on the same plan.

**244. Binary compounds** are compounds containing but two elements acting as elemental radicals.

There are also compounds constituted of but two elements which, strictly speaking, are *not* binary compounds because they clearly consist of compound radicals. Such compounds are met with mainly in organic chemistry, but examples are to be found also in inorganic chemistry. The chemistry of some of the compounds of carbon, nitrogen, oxygen and hydrogen belongs to both organic and inorganic chemistry.

Cyanogen is  $\text{NC.CN}$  and hence not strictly a binary compound; the fact that  $\text{N}_2\text{O}_2$  exists, which at a sufficiently high temperature is split up into molecules of NO, would seem to strongly indicate that  $\text{N}_2\text{O}_2$  is  $\text{ON.NO}$ ;  $\text{H}_2\text{O}_2$  is  $\text{HO.OH}$ ;  $\text{H}_2\text{S}_2$  is  $\text{HS.SH}$ , and hydrazine is  $\text{H}_2\text{N.NH}_2$ .

But the fluorides, chlorides, bromides and iodides, the oxides, sulphides, selenides and tellurides, the nitrides, phosphides, arsenides and antimonides, and the carbides and silicides, formed by elemental radicals, are truly binary compounds.

#### HALIDES.

**245.** The fluorides, chlorides, bromides and iodides are called **halides** (from *hals*, salt, and *eidos*, like) because the fluorides, chlorides, bromides and iodides of the metals are frequently of salt-like appearance and properties.

Fluorine, chlorine, bromine and iodine, *when exercising negative polarity*, are called *halogens* (from *hals*, salt, and *gennao*, to generate) because the compounds they form with the metals are halides.

*Positive* chlorine, bromine and iodine are not halogens.

But the halides of the metals are not *true* salts, their structure being entirely different from that of the compounds formed by the union of basic oxides with acidic oxides, or by reaction between basic oxides or hydroxides and the true acids or hydroxyl acids.

The fluorides, chlorides, bromides, and iodides of the non-metallic elements do not resemble salts in any respect, and the fluorides, chlorides, bromides and iodides of hydrogen have properties strongly resembling those of true acids and are accordingly called *hydrogen acids* or "hydracids."

Moreover, some compounds are formed by members of the chlorine family with other members of the same family.

**246. Fluorides.** All binary compounds containing fluorine are *fluorides*, for fluorine is of invariably negative chemical polarity.

The fluorides of greatest interest because of their uses are those of hydrogen and calcium. Hydrofluoric acid or hydrogen fluoride is made from "fluor spar" or calcium fluoride.

As all the halogens are univalent the molecular formulas of the fluorides are easily constructed:

HF is hydrogen fluoride or hydrofluoric acid;

CaF<sub>2</sub> is calcium fluoride;

SiF<sub>4</sub> is silicon tetrafluoride.

**247. Chlorides.** The binary chlorides are compounds formed by relatively positive elements with negative chlorine.

All compounds containing negative chlorine are chlorides.

As chlorine assumes positive polarity only when directly combined with oxygen, it follows that all binary chlorine compounds are chlorides except the oxides of chlorine.

The molecules of chlorides may contain from one to six chlorine atoms. As no single atom of any element can hold in combination more than six chlorine atoms, it follows that no binary chloride can contain more than six chlorine atoms in its molecule.

Monochlorides contain 1 chlorine atom.

Dichlorides contain 2 chlorine atoms.

Trichlorides contain 3 chlorine atoms.

Tetrachlorides contain 4 chlorine atoms.

Pentachlorides contain 5 chlorine atoms.

Hexachlorides contain 6 chlorine atoms.

**248.** The structures of binary chlorides is sufficiently illustrated by the following formulas, built on the system of chemical architecture we have learnt:

HCl, hydrogen chloride, or hydrochloric acid.

KCl, potassium chloride.

NaCl, sodium chloride (common "salt").

LiCl, lithium chloride.

AgCl, silver chloride.

CaCl<sub>2</sub>, calcium chloride.

SrCl<sub>2</sub>, strontium chloride.

SrCl<sub>2</sub>.6H<sub>2</sub>O, strontium chloride with water.

BaCl<sub>2</sub>, barium chloride.

BaCl<sub>2</sub>.2H<sub>2</sub>O, barium chloride with water.

MgCl<sub>2</sub>, magnesium chloride.

MgCl<sub>2</sub>.6H<sub>2</sub>O, magnesium chloride with water.

ZnCl<sub>2</sub>, zinc chloride.

FeCl<sub>2</sub>, ferrous chloride ("green chloride of iron" or the lower chloride of iron).

FeCl<sub>2</sub>.4H<sub>2</sub>O, ferrous chloride with water.

HgCl (or Hg<sub>2</sub>Cl<sub>2</sub>), mercurous chloride (calomel).

HgCl<sub>2</sub>, mercuric chloride (corrosive sublimate).

Cu<sub>2</sub>Cl<sub>2</sub>, cuprous chloride (lower chloride of copper).

CuCl<sub>2</sub>, cupric chloride (higher chloride of copper).

$\text{SnCl}_2$ , stannous chloride (chloride of tin).  
 $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , stannous chloride with water ("tin salt").  
 $\text{NCl}_3$ , nitrogen trichloride.  
 $\text{PCl}_3$ , phosphorus trichloride.  
 $\text{AlCl}_3$ , aluminum chloride.  
 $\text{SbCl}_3$ , antimonous chloride.  
 $\text{AuCl}_3$ , gold chloride (auric chloride, or gold trichloride).  
 $\text{PtCl}_4$ , platinic chloride, or platinum tetrachloride.  
 $\text{CCl}_4$ , carbon tetrachloride.  
 $\text{PCl}_5$ , phosphorus pentachloride.  
 $\text{WCl}_6$ , tungstic chloride, or tungsten hexachloride.  
 $\text{FeCl}_3$  (or  $\text{Fe}_2\text{Cl}_6$ ), ferric chloride ("sesquichloride," or the higher chloride, or "perchloride" of iron).  
 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (or  $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ ), ferric chloride with water.

**249.** The binary **bromides** are the compounds formed by other elements with negative bromine; hence all binary bromine compounds except its chloride.

Bromine has no oxides and no fluoride; but salts of hydroxyl acids of bromine are known, and in these the bromine exercises positive polarity (being directly united to the oxygen).

The structure of the binary bromides is perfectly analogous to that of the chlorides.

$\text{HBr}$  is hydrogen bromide, or hydrobromic acid.

$\text{KBr}$ , potassium bromide.

$\text{NaBr}$ , sodium bromide.

$\text{LiBr}$ , lithium bromide.

$\text{SrBr}_2$ , strontium bromide.

$\text{CaBr}_2$ , calcium bromide.

$\text{MgBr}_2$ , magnesium bromide.

$\text{ZnBr}_2$ , zinc bromide.

$\text{FeBr}_2$ , ferrous bromide.

$\text{AlBr}_3$ , aluminum bromide.

$\text{FeBr}_3$ , ferric bromide.

**250.** The binary **iodides** are the compounds formed by the union of negative iodine with other elements.

Iodine is positive with respect to oxygen, fluorine, chlorine and bromine. Hence the binary compounds of these elements with iodine are not iodides, but oxides, fluorides, chlorides and bromides.

The most important binary iodides are:

HI, hydrogen iodide, or hydriodic acid.

KI, potassium iodide.

NaI, sodium iodide.

LiI, lithium iodide.

AgI, silver iodide.

CaI<sub>2</sub>, calcium iodide.

SrI<sub>2</sub>, strontium iodide.

BaI<sub>2</sub>, barium iodide.

ZnI<sub>2</sub>, zinc iodide.

CdI<sub>2</sub>, cadmium iodide.

FeI<sub>2</sub>, ferrous iodide ("iodide of iron").

PbI<sub>2</sub>, lead iodide.

HgI (or Hg<sub>2</sub>I<sub>2</sub>), mercurous iodide (yellow iodide of mercury).

HgI<sub>2</sub>, mercuric iodide (red iodide of mercury).

S<sub>2</sub>I<sub>2</sub>, sulphur iodide.

AsI<sub>3</sub>, arsenous iodide ("iodide of arsenic").

#### OXIDES.

**251.** All binary compounds containing oxygen are oxides, because oxygen exercises negative polarity in relation to all other elements.

Fluorine is the only element which does not combine directly with oxygen.

Bromine combines directly with oxygen only in the formation of oxygen salts in which the bromine performs the acidic function, as in K<sub>2</sub>OBr<sub>2</sub> and in K<sub>2</sub>OBr.

Many elements combine with oxygen in more than one proportion, or have more than one oxide each.

Oxides containing a larger proportion of oxygen are called *higher oxides*, and those containing a less proportion of oxygen are called *lower oxides*.

**252.** The types of the oxides of the elements are eight. As oxygen is bivalent the eight different kinds of oxides are clearly seen and compared by the employment of symbolic formulas in which one atom of the element uniting with the oxygen is represented by R. The typical formulas are then as follows:

1. R<sub>2</sub>O, representing the normal oxides of monads.

2. RO (or R<sub>2</sub>O<sub>2</sub>), representing the normal oxides of dyads.

3.  $R_2O_3$  is the structure of the oxides of triads.
4.  $RO_2$  (or  $R_2O_4$ ), the oxides of tetrads.
5.  $R_2O_5$ , the formula of the oxides of pentads.
6.  $RO_3$  (or  $R_2O_6$ ), representing the oxides of hexads.
7.  $R_2O_7$ , showing the structure of the oxides of heptads.
8.  $RO_4$  (or  $R_2O_8$ ), which is the type of the highest oxides known, namely, those of the octads.

A comparison of these several types is most striking when the formula is constructed with two atoms of the positive element, for then it is seen that these two atoms are united with 1, or 2, 3, 4, 5, 6, 7 or 8 atoms of oxygen, according to the valence exercised by the element united to the oxygen. [This accounts for the eight groups of the periodic system, and the eight groups of elemental radicals classified according to their respective maximum positive valences.]

**253.** Elements having a variable valence show their highest valence in their oxygen compounds.

No one atom of any element can unite directly with more than 4 oxygen atoms, for no atom can hold in combination more than 8 bonds.

The only oxides of the type  $RO_4$  known to exist are those of ruthenium and osmium.

**254.** The structure of binary oxides is sufficiently illustrated by the following examples:

$H_2O$ , hydrogen oxide or water.

$K_2O$ , potassium oxide.

$Na_2O$ , sodium oxide.

$Li_2O$ , lithium oxide.

$Ag_2O$ , silver oxide.

$Hg_2O$ , mercurous oxide.

$Cu_2O$ , cuprous oxide.

$BaO$ , barium oxide.

$SrO$ , strontium oxide.

$CaO$ , calcium oxide.

$MgO$ , magnesium oxide.

$ZnO$ , zinc oxide.

$FeO$ , ferrous oxide.

$MnO$ , manganous oxide.

$PbO$ , lead oxide.

CuO, cupric oxide.  
HgO, mercuric oxide.  
NO (or  $N_2O_2$ ), nitric oxide.  
CO, carbon monoxide.  
 $Al_2O_3$ , aluminum oxide.  
 $Fe_2O_3$ , ferric oxide.  
 $Bi_2O_3$ , bismuth oxide.  
 $As_2O_3$  (or  $As_2O_5$ ), arsenous oxide.  
 $Sb_2O_3$ , antimonous oxide.  
 $MnO_2$ , manganese dioxide.  
 $PbO_2$ , lead dioxide.  
 $CO_2$ , carbon dioxide.  
 $SO_2$ , sulphur dioxide.  
 $NO_2$  (or  $N_2O_4$ ), nitrogen peroxide.  
 $N_2O_5$ , nitrogen pentoxide.  
 $P_2O_5$ , phosphorus pentoxide.  
 $SO_3$ , sulphur trioxide.  
 $CrO_3$ , chromic anhydride.  
 $Mn_2O_7$ , manganese heptoxide.  
 $OsO_4$ , osmium tetroxide.

**255.** With respect to their chemical behavior the oxides are of three kinds: 1, basic oxides; 2, acidic oxides; and 3, indifferent oxides (including all "peroxides").

The basic and acidic oxides have the power to form salts and are, therefore, sometimes called *saline oxides*. **Basic oxides** form salts with the acidic oxides or with acids, and the **acidic oxides** form salts with the basic oxides or with basic hydroxides.

Some oxides (and hydroxides) are both acidic and basic, as, for instance,  $ZnO$ ,  $Al_2O_3$ , etc. They are acidic toward bases, but basic toward acids.

The **indifferent oxides** are those that form neither acids, bases, nor salts.

The relations of the oxides to acids, bases and salts will be treated of in a separate chapter.

#### SULPHIDES.

**256.** The binary **sulphides** include all binary sulphur compounds except those formed by the halogens and by oxygen, and sulphur salts containing both positive and negative sulphur.

All compounds containing only negative sulphur are sulphides; but the binary compounds formed by sulphur with oxygen are oxides, and the binary sulphur compounds of the halogens are the chlorides, bromides and iodides of sulphur.

**257.** The striking analogies between sulphides and oxides are forcibly illustrated by the fact that one class of sulphides correspond in structure and behavior to the acid-forming oxides, another class of sulphides correspond to the basic oxides, and these two kinds of sulphides are capable of combining with each other to form salts which differ from the oxygen salts as to structure only in that they contain sulphur instead of oxygen.

A third class of sulphides correspond to the indifferent oxides, being incapable of forming salts.

**258.** The structure of binary sulphides is illustrated by the following examples:

$\text{H}_2\text{S}$ , hydrogen sulphide ("sulphuretted hydrogen").

$\text{K}_2\text{S}$ , potassium sulphide.

$\text{Na}_2\text{S}$ , sodium sulphide.

$\text{CaS}$ , calcium sulphide.

$\text{ZnS}$ , zinc sulphide.

$\text{FeS}$ , ferrous sulphide.

$\text{HgS}$ , mercuric sulphide.

$\text{CuS}$ , cupric sulphide.

$\text{PbS}$ , lead sulphide (plumbic).

$\text{CS}_2$ , carbon disulphide ("bisulphide of carbon").

$\text{As}_2\text{S}_3$ , arsenous sulphide (arsenic trisulphide).

$\text{Sb}_2\text{S}_3$ , antimonous sulphide (antimony trisulphide).

$\text{As}_2\text{S}_5$ , arsenic sulphide (arsenic pentasulphide).

$\text{Sb}_2\text{S}_5$ , antimonic sulphide (antimony pentasulphide).

#### OTHER BINARY COMPOUNDS.

**259. Nitrides** are the compounds containing nitrogen as a negative radical. The nitride of hydrogen is called *ammonia* and its molecular formula is  $\text{H}_3\text{N}$  (commonly written  $\text{NH}_3$ ). Ammonia is a gas which is readily taken up by water, and the water-solution is regarded as containing ammonium hydroxide,  $\text{H}_4\text{NOH}$ . Ammonia and ammonium hydroxide possess a peculiar strong, suffocating odor and have strongly alkaline properties.

**260. Phosphides** are formed by hydrogen and some of the metals with negative phosphorus. The gas called *phosphine*, or hydrogen phosphide,  $H_3P$ , is perfectly analogous to hydrogen nitride, or ammonia, as to its structure. (It was formerly called "phosphoretted hydrogen.") But hydrogen phosphide is scarcely alkaline, for although "phosphonium" compounds exist which correspond to the ammonium compounds, such compounds are rare and comparatively unstable.

Zinc phosphide,  $Zn_3P_2$ , has been used in medicine to a limited extent. It is a grayish-black hard solid, insoluble in water.

**261. Carbides** are formed by positive elements with negative carbon.

*Marsh gas*, or methane, is a carbide of hydrogen.

Calcium carbide,  $CaC_2$ , is an important compound employed for the production of acetylene gas,  $C_2H_2$ . The calcium carbide is a gray, friable solid which at once decomposes when brought into contact with water.

Iron carbide is contained in cast iron.

**262.** Binary inorganic compounds which do not fall within the groups mentioned in the preceding paragraphs are of no special importance to the pharmacist. A few which possess theoretical interest are mentioned elsewhere in this book for purposes of illustration or instruction.

#### COMPOUNDS CLOSELY RESEMBLING THOSE OF BINARY COMPOSITION.

**263.** The compounds called cyanides, ferrocyanides, ferricyanides, and oxychlorides resemble the binary compounds in general structure so much that they must be mentioned here. Cyanogen, ferrocyanogen and ferricyanogen are compound negative radicals, which have been called compound halogens because they form compounds closely analogous to those formed by fluorine, chlorine, bromine and iodine.

There are also a number of compounds formed by the halogens with certain compound positive radicals and which correspond to the other cyanides, ferrocyanides and ferricyanides.

All of these compounds might be designated as compound halides.

Finally, there are a number of so-called oxychlorides, oxybromides, oxyiodides, etc., which resemble the binary compounds.

**264. Cyanides** are the compounds containing the characteristic "compound halogen" called cyanogen. This negative radical is composed of one atom of carbon united to one atom of nitrogen. It is sometimes written CN, but more conveniently represented by the symbol Cy. As carbon is a tetrad and nitrogen a triad, it follows that CN is a monad having one free carbon bond, and that bond is of negative polarity in relation to the radicals which form cyanides.

HCy is hydrogen cyanide, or hydrocyanic acid.

KCy is potassium cyanide.

AgCy is silver cyanide.

HgCy<sub>2</sub> is mercuric cyanide.

**265. Ferrocyanides** are assumed to contain the quadrivalent negative radical FeCy<sub>6</sub>. The real structure of ferrocyanides is, however, uncertain. K<sub>4</sub>FeCy<sub>6</sub>·3H<sub>2</sub>O is potassium ferrocyanide. Fe<sub>4</sub>(FeCy<sub>6</sub>)<sub>3</sub> is ferric ferrocyanide.

**266. Ferricyanides** are assumed to contain the sexivalent negative radical Fe<sub>2</sub>Cy<sub>12</sub>.

K<sub>3</sub>Fe<sub>2</sub>Cy<sub>12</sub> is potassium ferricyanide. [It is frequently written K<sub>3</sub>FeCy<sub>6</sub>.]

**267.** Other compound halides of pharmaceutical interest are:

H<sub>4</sub>NCl, ammonium chloride.

H<sub>4</sub>NBr, ammonium bromide.

H<sub>4</sub>NI, ammonium iodide.

H<sub>2</sub>HgNCl, mercurammonium chloride.\*

H<sub>4</sub>NCy, ammonium cyanide.

**268. Oxychloride** of bismuth and oxychloride of antimony are apparently normal chlorides of the compound radicals bismuthyl, BiO, and antimonyl, SbO, respectively.

But there are other oxychlorides or "basic chlorides" the composition of which is not well understood. They *seem* to consist of metallic chlorides united to the oxides or hydroxides of the same metals, but are of variable composition. The basic ferric chloride, which is frequently formed in solutions of ferric chloride, is an example; another is the oxychloride of mercury

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\*"Ammoniated mercury" may also be regarded as mercuric chloramide, H<sub>2</sub>NHgCl, instead of mercurammonium chloride.

sometimes formed in the decomposition of mercuric chloride with an insufficient amount of alkali hydroxide.

ONCl is nitrosyl chloride.

OBiCl is bismuthyl chloride.

OSbCl is antimonyl chloride.

OFeCl is ferryl chloride.

## CHAPTER XIII.

### HYDROXIDES, ACIDS AND BASES.

**269.** The *hydroxides* are highly important and interesting compounds formed by positive radicals with the negative compound radical HO or OH, called *hydroxyl*.

As hydrogen is a positive monad and oxygen a negative dyad, it follows that hydroxyl must be a negative monad having one free oxygen bond by which it holds a positive radical in combination.

**270.** The **normal hydroxides** of the elements are molecules composed of but three kinds of atoms, two of which are hydrogen and oxygen directly united to each other in the form of hydroxyl, the third element being directly united to all of the oxygen atoms of that hydroxyl. A normal hydroxide accordingly contains no other oxygen except that of the hydroxyl, and the number of oxygen atoms in any normal hydroxide must be the same as the number of hydrogen atoms in it.

**271.** Elements of variable valence may have more than one normal hydroxide.

Iron has two normal hydroxides, the ferrous hydroxide,  $\text{Fe}(\text{OH})_2$ , and the ferric hydroxide,  $\text{Fe}(\text{OH})_3$ .

Chlorine has four normal hydroxides, namely,  $\text{ClOH}$ ,  $\text{Cl}(\text{OH})_3$ ,  $\text{Cl}(\text{OH})_5$ , and  $\text{Cl}(\text{OH})_7$ .

Nitrogen has three normal hydroxides:  $\text{NOH}$ ,  $\text{N}(\text{OH})_3$ , and  $\text{N}(\text{OH})_5$ .

Sulphur has three, namely,  $\text{S}(\text{OH})_2$ ,  $\text{S}(\text{OH})_4$ , and  $\text{S}(\text{OH})_6$ .

**272.** **Meta-hydroxides** are formed when hydrogen and oxygen are split off from normal hydroxides, the hydrogen and oxygen thus separated being always in the proportions required to form water, and, indeed, they always combine to produce that compound. Thus  $\text{OFeOH}$  is formed together with one molecule of water out of  $\text{Fe}(\text{OH})_3$ .

Meta-hydroxides accordingly contain a larger number of oxygen atoms than of hydrogen atoms.

But the water formed when normal hydroxides are changed to meta-hydroxides may be formed from hydrogen and oxygen

separated from the hydroxyl of more than one molecule of the normal hydroxide. Thus  $\text{H}_4\text{P}_2\text{O}_7$  and  $3\text{H}_2\text{O}$  are produced by  $2\text{H}_5\text{PO}_3$ .

**273.** The hydroxides of basic or base-forming elements are *bases*, and the hydroxides of acidic or acid-forming elements are *acids*.

Water, or hydrogen hydroxide,  $\text{HOH}$ , may be regarded as the connecting link between acidic and basic hydroxides. If one of its hydrogen atoms be replaced by a metal capable of performing basic functions the new hydroxide thus formed is a base and forms salts with acids, while if one atom of the hydrogen be replaced by any element of acidic functions the resulting new hydroxide is an acid and can form salts with bases. And if both hydrogen atoms of  $\text{HOH}$  be replaced, one by an element of basic functions and the other by an element of acidic functions, the product will be a salt.

**274.** The structure of normal hydroxides may be seen in the following table:

$\text{HOH}$ , hydrogen hydroxide, or water.

$\text{KOH}$ , potassium hydroxide.

$\text{NaOH}$ , sodium hydroxide.

$\text{LiOH}$ , lithium hydroxide.

$\text{H}_4\text{NOH}$ , ammonium hydroxide.

$\text{Ca}(\text{OH})_2$ , calcium hydroxide.

$\text{Ba}(\text{OH})_2$ , barium hydroxide.

$\text{Sr}(\text{OH})_2$ , strontium hydroxide.

$\text{Mg}(\text{OH})_2$ , magnesium hydroxide.

$\text{Zn}(\text{OH})_2$ , zinc hydroxide.

$\text{Fe}(\text{OH})_2$ , ferrous hydroxide.

$\text{Fe}(\text{OH})_3$ , ferric hydroxide.

$\text{Al}(\text{OH})_3$ , aluminum hydroxide.

$\text{Bi}(\text{OH})_3$ , bismuth hydroxide.

[Metallic hydroxides were formerly called "hydrates" and "hydrated oxides," and are still called so by many; but true hydrates contain water—not hydroxyl.]

$\text{ClOH}$  is the hydroxide of univalent chlorine.

$\text{N}(\text{OH})_3$  is the hydroxide of trivalent nitrogen.

$\text{B}(\text{OH})_3$  is the hydroxide of trivalent boron.

$\text{C}(\text{OH})_4$  is the hydroxide of tetravalent carbon.

$\text{S}(\text{OH})_6$  is the hydroxide of hexavalent sulphur.

## ACIDS.

**275.** The inorganic acids are hydrogen compounds which form salts when their hydrogen is replaced by metallic elements.

There are two distinct classes of inorganic acids: 1, the *hydrogen acids*; and the *hydroxyl acids*.

**276.** The **hydrogen acids**, or "hydracids," are few, for they are the compounds formed by hydrogen with the halogens.

When the hydrogen of a hydrogen acid is replaced by a metal the new molecule thus obtained is a halide.

The structure of the hydrogen acids is very simple because hydrogen and the halogens are of the same valence.

Including that formed by the "compound halogen" called cyanogen, we have five well-known hydrogen acids, namely:

HF, hydrofluoric acid, or hydrogen fluoride.

HCl, hydrochloric acid, or hydrogen chloride.

HBr, hydrobromic acid, or hydrogen bromide.

HI, hydriodic acid, or hydrogen iodide.

HCN (or HCy), hydrocyanic acid, or hydrogen cyanide.

[Not all chemists recognize these compounds as acids. Those who do not call them acids refer to them as the halides of hydrogen and reserve the title of acid for the acidic hydroxides.]

**277.** The **hydroxyl acids** are the normal hydroxides and the meta-hydroxides of elements exercising acidic functions.

In other words they are the acidic hydroxides.

They are the compounds formed by acidic or acid-forming elements with hydroxyl.

[Many chemists regard the hydroxyl acids as the only "true acids."]

The hydroxyl acids are often called "oxygen acids" to distinguish them from the "hydrogen acids" which contain no oxygen; but, as both classes of acids contain hydrogen, the title hydroxyl acid is more explicit and significative. Hydroxyl acids are frequently also called "oxy-acids."

**278.** From the fact that the inorganic hydroxyl acids are the acidic hydroxides and meta-hydroxides the student will readily understand that they are composed of but three elements, namely, hydrogen, oxygen and the acid-forming element.

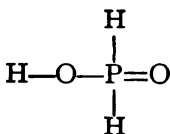
*Normal hydroxyl acids* are the normal hydroxides of the acid-

forming elements, and the *meta-acids* are their meta-hydroxides.

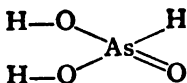
Hence the molecules of all normal acids contain the same number of hydrogen atoms as of oxygen atoms, while the molecules of all meta-acids contain a larger number of oxygen atoms than of hydrogen atoms.

**279.** Nearly all inorganic acids can exchange all of their hydrogen for some metal, thereby forming salts. But there are a few inorganic hydroxyl acids which contain non-replaceable hydrogen. The molecular formulas of such acids are, therefore, so written as to indicate that fact, for their molecular structure must be different from that of the other inorganic hydroxyl acids.

Hypophosphorous acid is not  $\text{H}_3\text{PO}_2$ , nor  $\text{HH}_2\text{PO}_2$ , but rather  $\text{HPO}_2\text{H}_2$  or  $\text{HPH}_2\text{O}_2$  because it contains only one hydroxyl group and hence only one replaceable hydrogen atom, and its molecular structure is probably



Arsenous acid is probably  $\text{H}_2\text{AsHO}_3$ , rather than  $\text{H}_3\text{AsO}_3$ , because only two of its hydrogen atoms can be exchanged for metals, and its structure is probably



Phosphorous acid, too, is probably  $(\text{HO})_2\text{PHO}$ , or  $\text{H}_2\text{PHO}_3$ , and its structure analogous to that of arsenous acid.

**280.** As many metallic salts of the organic acids are necessarily treated of in connection with inorganic chemistry, the student should know that those organic acids are all hydroxyl acids, but that their hydroxyl is invariably united to the compound radical  $\text{CO}$ , called *carbonyl*, so that they contain  $\text{CO.OH}$ , called "carboxyl." Organic acids also contain other atomic groups which may include hydrogen, and the hydrogen not contained in the  $\text{CO.OH}$  is not basic and can not be exchanged for metal. An organic acid, therefore, nearly always contains both basic and non-basic. *hydrogen*

281. The most common hydroxyl acids are given in this table, including some organic acids.

Some of the acids mentioned are known only by their salts, and others are assumed on theoretical grounds to exist although their salts are unknown (as for instance  $\text{H}_6\text{SO}_6$ ).

<i>Name of Acid.</i>	<i>Formula showing the number of hydroxyl groups.</i>	<i>Common molecular formula.</i>
<b>MONOBASIC ACIDS.</b>		
Acetic acid .....	$\text{HO.CO.CH}_3$	$\text{HC}_2\text{H}_3\text{O}_2$
Benzoic acid .....	$\text{HO.C}_6\text{H}_5\text{O}$	$\text{HC}_7\text{H}_5\text{O}_2$
Chloric acid .....	$\text{HO.ClO}_2$	$\text{HClO}_3$
Hypochlorous acid .....	$\text{HO.Cl}$	$\text{HClO}$
Hypophosphorous acid .....	$\text{HO.PH}_2\text{O}$	$\text{H}_3\text{P}_2\text{O}_4$
Iodic acid .....	$\text{HO.IO}_2$	$\text{HIO}_3$
Lactic acid .....	$\text{HO.C}_3\text{H}_5\text{O}_2$	$\text{HC}_3\text{H}_5\text{O}_3$
"Metaphosphoric acid" (glacial) ..	$\text{HO.PO}_2$	$\text{HPO}_3$
Nitric acid .....	$\text{HO.NO}_2$	$\text{HNO}_3$
Nitrous acid .....	$\text{HO.NO}$	$\text{HNO}_2$
Oleic acid .....	$\text{HO.C}_{18}\text{H}_{33}\text{O}$	$\text{HC}_{18}\text{H}_{33}\text{O}_2$
Perchloric acid .....	$\text{HO.ClO}_3$	$\text{HClO}_4$
Permanganic acid .....	$\text{HO.MnO}_2$	$\text{HMnO}_4$
Phenylsulphonic acid .....	$\text{HO.C}_6\text{H}_5\text{SO}_2$	$\text{HC}_6\text{H}_5\text{SO}_3$
Salicylic acid .....	$\text{HO.C}_6\text{H}_4\text{O}_2$	$\text{HC}_7\text{H}_5\text{O}_3$
Valeric acid .....	$\text{HO.C}_5\text{H}_9\text{O}$	$\text{HC}_5\text{H}_9\text{O}_2$
<b>BIBASIC ACIDS.</b>		
Arsenous acid .....	$(\text{HO})_2.\text{AsHO}$	$\text{H}_2\text{AsHO}_2$
Carbonic acid .....	$(\text{HO})_2.\text{CO}$	$\text{H}_2\text{CO}_3$
Chromic acid .....	$(\text{HO})_2.\text{CrO}_2$	$\text{H}_2\text{CrO}_4$
Dichromic acid .....	$(\text{HO})_2.\text{Cr}_2\text{O}_3$	$\text{H}_2\text{Cr}_2\text{O}_7$
Oxalic acid .....	$(\text{HO}_2).( \text{CO} )_2$	$\text{H}_2\text{C}_2\text{O}_4$
Phosphorous acid .....	$(\text{HO})_2.\text{PHO}$	$\text{H}_2\text{PHO}_3$
Sulphuric acid .....	$(\text{HO})_2.\text{SO}_2$	$\text{H}_2\text{SO}_4$
Sulphurous acid .....	$(\text{HO})_2.\text{SO}$	$\text{H}_2\text{SO}_3$
Tartaric acid .....	$(\text{HO})_2.\text{C}_2\text{H}_2\text{O}_4$	$\text{H}_2\text{C}_2\text{H}_2\text{O}_6$
Tetraboric acid .....	$(\text{HO})_2.\text{B}_2\text{O}_3$	$\text{H}_2\text{B}_2\text{O}_7$
Thiosulphuric acid .....	$(\text{HO})_2.\text{SOS}$	$\text{H}_2\text{SO}_3\text{S}$
<b>TRIBASIC ACIDS.</b>		
Boric acid .....	$(\text{HO})_3.\text{B}$	$\text{H}_3\text{BO}_3$
Citric acid .....	$(\text{HO})_3.\text{C}_6\text{H}_7\text{O}_4$	$\text{H}_3\text{C}_6\text{H}_7\text{O}_7$
Arsenic acid .....	$(\text{HO})_3.\text{AsO}$	$\text{H}_3\text{AsO}_4$
Phosphoric acid .....	$(\text{HO})_3.\text{PO}$	$\text{H}_3\text{PO}_4$
<b>TETRABASIC ACIDS.</b>		
Carbonic acid, Normal .....	$(\text{HO})_4.\text{C}$	$\text{H}_4\text{CO}_4$
Monometasulphuric acid .....	$(\text{HO})_4.\text{SO}$	$\text{H}_4\text{SO}_6$
Pyroarsenic acid .....	$(\text{HO})_4.\text{As}_2\text{O}_5$	$\text{H}_4\text{As}_2\text{O}_7$
Pyrophosphoric acid .....	$(\text{HO})_4.\text{P}_2\text{O}_5$	$\text{H}_4\text{P}_2\text{O}_7$
Normal Nitric acid .....	$(\text{HO})_4.\text{N}$	$\text{H}_4\text{NO}_4$
Normal Sulphuric acid .....	$(\text{HO})_4.\text{S}$	$\text{H}_4\text{SO}_6$

282. The only negative bonds in the molecule of any inorganic hydroxyl acid are its oxygen bonds. The polarity-value of the acidic or acid-forming element is, therefore, found by deducting the total number of the hydrogen atoms from the total number

of oxygen bonds (or from twice the number of oxygen atoms) in the molecule.

**283. Acid-residues.** When the replaceable hydrogen of a hydroxyl acid is removed from its molecular formula all that remains constitutes what is conveniently called the *acid-residue* of that acid.

The molecular formula of nitric acid being  $\text{HNO}_3$  its acid-residue is  $\text{NO}_3$ . The sulphuric-acid-residue is  $\text{SO}_4$ , because the molecular formula of sulphuric acid is  $\text{H}_2\text{SO}_4$ .

[The acid-residues are also called "acid-radicals," and "negative salt-radicals."]

**284.** The *basicity* of any acid is expressed by the number of replaceable basic hydrogen atoms in its molecular, or the number of hydroxyl groups it contains, or by the valence of its residue.

*Monobasic acids* are acids containing only one basic hydrogen atom. Their acid-residues accordingly are monads.

*Bibasic acids* are those that contain two basic hydrogen atoms, and whose residues, therefore, are bivalent.

*Tribasic acids* are acids containing three hydroxyl groups and hence three basic hydrogen atoms. Their residues are trivalent.

*Tetrabasic acids* have four basic or replaceable hydrogen atoms, and their residues are tetrads.

[All "hydrogen acids" are, of course, monobasic.]

#### BASES.

**285.** The inorganic **bases** are the hydroxides of metals performing basic functions.

In other words they are metallic hydroxides which have the power to form salts with the acids.

When a base and an acid react with each other two products are formed—a salt and water. The metal of the base and the replaceable hydrogen (the hydrogen of the hydroxyl) of the acid exchange places, whereby the metal turns the acid into a salt and the hydrogen of the acid combines with the hydroxyl of the base to form hydrogen hydroxide or water.

[But many chemists include the basic oxides under the head of bases, and even the metals performing basic functions are often referred to as bases.]

**286. Alkalies.** The most powerful of all bases are the hy-

droxides of the "alkali metals" cæsium, rubidium, potassium, sodium and lithium, in the order named. The hydroxide of the compound radical ammonium,  $\text{H}_4\text{N}$ , is also called an alkali.

The alkalies differ from the other bases in that they are freely water-soluble (except that lithium hydroxide is not as freely soluble as the other alkalies).

**287.** Most of the inorganic bases are normal hydroxides. But *meta-bases* also exist. They are the basic meta-hydroxides. These are formed in the same manner as meta-acids are formed.

The meta-bases or basic meta-hydroxides are unfortunately called "basic hydroxides," which is unscientific in view of the fact that all bases are basic hydroxides because they all perform basic functions and that the most powerful bases are normal hydroxides, whereas some of metallic meta-hydroxides do not form normal salts or are acted upon by acids only with difficulty.

**288. Base-residues.** When the replaceable hydrogen is removed from the molecular formula of any base, the remainder is the *base-residue*. Thus the base-residue of  $\text{KOH}$  is  $\text{KO}$ , and that of  $\text{Ca}(\text{OH})_2$  is  $\text{CaO}_2$ .

## CHAPTER XIV.

### SALTS.

**289. Salts.** An inorganic salt is a compound formed by a metal with an acid-residue.

The metal is the positive salt-forming radical, and the acid-residue the negative salt-forming radical of any metallic oxygen salt.

**290.** At least three elements are contained in the molecule of an inorganic oxygen salt, namely: 1, the metal which performs the basic function; 2, oxygen; and 3, the element performing the acidic function. But some inorganic salts contain four elements.

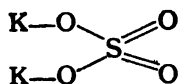
Two elements may perform the basic function as in double-salts and acid salts; and the oxygen may be partly replaced by sulphur, as in the thiosulphates.

The oxygen, or a part of it, performs a *linking function*, indirectly uniting the metal to the acidic element.

The following examples illustrate these several features of salt structure:

$\text{NaOCl}$  (commonly written  $\text{NaClO}$ ) is a very simple salt molecule in which Na performs the basic function; Cl is the acidic element; and the Na and Cl, both univalent, are linked together by the bivalent oxygen.

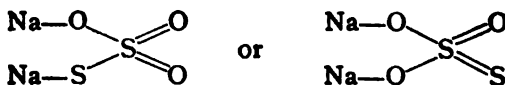
In  $\text{K}_2\text{SO}_4$  which is  $(\text{KO})_2\text{SO}_2$ , or



K is the basic element, S the acidic element, two of the oxygen atoms perform the linking function, and the other two oxygen atoms are united *only to the acidic element*.

In  $\text{KHSO}_4$  we find that both K and H perform the basic function, and in  $\text{KNaC}_4\text{H}_4\text{O}_6$  that function is exercised by K and Na.

In sodium thiosulphate, which is



the sodium is the basic element, which is linked to the acidic (positive) sulphur atom by means of two linking oxygen atoms, while the third oxygen atom and the second sulphur atom (negative sulphur, taking the place of oxygen) are united directly only to the acidic sulphur.

**291.** Salts analogous to the normal acids contain no oxygen except that which links the basic element and the acidic element together. Thus all of the oxygen in  $\text{NaOCl}$ , and in  $\text{AlHO}_4\text{Si}$ , is linking oxygen.

But the meta-acids form salts in which only a portion of the oxygen performs the linking function.

The student will readily understand this difference between the salts of normal acids and the salts of meta-acids from the fact that all of the oxygen of the hydroxyl of any acid is linking oxygen in the molecule of the acid as well as the salt, and that no other oxygen of the acid except that of its hydroxyl performs the linking function.

**292.** Whenever any metallic salt consists of but three elements, the oxygen is the only element of negative polarity in the molecule, and the oxygen bonds constitute one-half of all the bonds in the whole molecule. The bonds of the other elements of the salt molecule are all of positive polarity.

[ $\text{HPO}_2\text{H}_2$  and  $\text{H}_2\text{AsHO}_3$  are exceptions.]

**293.** The salts formed by, or analogous to, the hydroxyl acids are by many chemists regarded as the only true salts, and they are the only class of salts referred to in the preceding paragraphs.

But the metallic halides and the halides of ammonium are often called "salts," and there are, moreover, a class of compounds properly called "sulphur salts," which differ from the oxygen salts only in that they contain negative sulphur in place of oxygen, and several kinds of organic salts. It is, therefore, best to designate the metallic salts of the inorganic hydroxyl acids as inorganic *oxygen salts* to distinguish them from all other kinds of compounds called salts.

**294.** The only difference between the structure of an acid and its metallic salts is that hydrogen is the basic element of the acid, whereas the basic element of a metallic salt of that acid is a metal, as the following examples will show:

<i>Acids.</i>	<i>Salts.</i>
HOCl	NaOCl
Hypochlorous acid	Sodium hypochlorite.
	Ca(OCl) <sub>2</sub>
	Calcium hypochlorite.
HNO <sub>3</sub> , or HONO <sub>2</sub> .	KNO <sub>3</sub> , or KONO <sub>2</sub> .
Nitric acid.	Potassium nitrate.
H <sub>2</sub> SO <sub>4</sub> , or (HO) <sub>2</sub> SO <sub>2</sub>	Na <sub>2</sub> SO <sub>4</sub> , or (NaO) <sub>2</sub> SO <sub>2</sub> .
Sulphuric acid.	Sodium sulphate.
	BaSO <sub>4</sub> , or BaO <sub>2</sub> SO <sub>2</sub> .
	Barium sulphate.

**295.** From the foregoing statements it is clear that oxygen salts of the metals are produced when the basic ("replaceable") hydrogen of any acid is replaced by a metal; or when the hydroxyl of an acid is replaced by a base-residue; or when the oxygen of a basic oxide is replaced by an acid-residue; or when the hydroxyl of a base is replaced by an acid-residue.

**296.** Among the most important groups of metallic oxygen salts are the following:

<i>Names.</i>	<i>Characteristic Negative Salt-forming Radical or Acid-residue.</i>	<i>By what acid formed.</i>
Sulphates .....	O <sub>2</sub> SO <sub>2</sub> or SO <sub>4</sub>	Sulphuric acid.
Sulphites .....	O <sub>2</sub> SO or SO <sub>3</sub>	Sulphurous acid.
Thiosulphates .....	O <sub>2</sub> SOS or S <sub>2</sub> O <sub>3</sub>	Thiosulphuric acid.
Chlorates .....	OCLO <sub>2</sub> or ClO <sub>3</sub>	Chloric acid.
Hypochlorites .....	OCl or ClO	Hypochlorous acid.
Nitrates .....	ONO <sub>2</sub> or NO <sub>3</sub>	Nitric acid.
Nitrites .....	ONO or NO <sub>2</sub>	Nitrous acid.
Phosphates ("ortho")...	O <sub>2</sub> PO or PO <sub>4</sub>	Phosphoric acid.
Metaphosphates .....	OPO <sub>2</sub> or PO <sub>3</sub>	Metaphosphoric acid.
Pyrophosphates .....	O <sub>4</sub> P <sub>2</sub> O <sub>7</sub> or P <sub>2</sub> O <sub>7</sub>	Pyrophosphoric acid.
Hypophosphites .....	OPH <sub>2</sub> O or PH <sub>2</sub> O <sub>2</sub>	Hypophosphorous acid.
Carbonates .....	O <sub>2</sub> CO or CO <sub>3</sub>	Carbonic acid.
Pyroborates .....	O <sub>2</sub> B <sub>2</sub> O <sub>5</sub> or B <sub>2</sub> O <sub>7</sub>	Tetraboric acid.
Arsenates ("ortho")...	O <sub>2</sub> AsO or AsO <sub>4</sub>	Arsenic acid.
Arsenites .....	O <sub>2</sub> AsHO or AsHO <sub>3</sub>	Arsenous acid.
Permanganates .....	OMnO <sub>3</sub> or MnO <sub>4</sub>	Permanganic acid.
Acetates .....	OCOCH <sub>3</sub> or C <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	Acetic acid.
Oxalates .....	O <sub>2</sub> (CO) <sub>2</sub> or C <sub>2</sub> O <sub>4</sub>	Oxalic acid.
Tartrates .....	O <sub>2</sub> C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> or C <sub>2</sub> H <sub>2</sub> O <sub>4</sub>	Tartaric acid.
Citrates .....	O <sub>2</sub> C <sub>6</sub> H <sub>7</sub> O <sub>4</sub> or C <sub>6</sub> H <sub>7</sub> O <sub>7</sub>	Citric acid.

The student will observe that the oxygen atoms placed first in the formulas in the second column are the linking oxygen atoms and their number indicates in each case the number of hydroxyl groups or of replaceable hydrogen atoms contained in the acid,

and hence the valence of the acid-radical or acid-residue (or the basicity of the acid).

**297.** As the hydroxyl acids may contain from one to six hydroxyl groups, although the most common acids generally contain but one or two, it follows that if the basic hydrogen atoms are not all replaced by metallic elements the resulting salts must still contain hydroxyl.

Salts containing no remaining basic hydrogen are generally termed "normal salts."

[The student is warned against any confusion of ideas concerning the salts of "normal acids" and the normal salts of any acids.]

Salts that do contain remaining basic hydrogen are called "acid salts."

Each acid can form but one normal salt with each basic metal.

The basic metal is the only basic element in any normal metallic salt.

**298.** Monobasic acids can form only normal salts.

Bibasic acids can form two kinds of salts—normal salts in which there is no basic hydrogen left, and acid salts in which one of the two replaceable hydrogen atoms has been exchanged for a metal while the other is retained.

Tribasic acids may have three kinds of salts, according to the number of hydrogen atoms replaced by metallic elements—one normal salt and two kinds of acid salts.

**299.** A **primary salt** is the salt formed when an acid exchanges but one of its hydrogen atoms for a metallic element.  $\text{NaNO}_3$ ,  $\text{KHCO}_3$ ,  $\text{NaH}_2\text{PO}_4$ , and  $\text{Pb}(\text{NO}_3)_2$  are all primary salts.

All the salts of monobasic acids are primary salts.

**Secondary salts** are formed by the replacement of two hydrogen atoms of the acid by metal, as  $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{HPO}_4$ .

**Tertiary salts** are formed when three basic hydrogen atoms are replaced by metal, as in  $\text{K}_3\text{C}_6\text{H}_5\text{O}_7$ .

**300.** **Double-salts** are the salts formed when two or more of the basic hydrogen atoms of an acid are exchanged for two metals.

Tartaric acid is  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ ; hence  $\text{KNaC}_4\text{H}_4\text{O}_6$  is a double salt formed by the exchange of one hydrogen atom for potassium and the other for sodium.

$KAl(SO_4)_2 \cdot 12H_2O$  is the double salt commonly known as "alum."

$H_4NFe(SO_4)_2 \cdot 12H_2O$  is another double salt called "iron alum."

**301. Basic salts or Meta-salts.** By a "basic" metallic salt is meant a compound *apparently* composed of a normal metallic salt together with the oxide or hydroxide of the same metal, and many so-called basic salts are customarily represented by double molecular formulas on the assumption that saturated molecules can combine with each other. Thus the pharmacopœias usually represent the common magnesium carbonate as  $Mg(CO_3)_4 \cdot Mg(OH)_2$  and yellow sulphate of mercury, as  $(HgO)_2 \cdot HgSO_4$ .

But it is inconsistent with accepted chemical hypotheses to assume that saturated molecules can enter into true chemical combination with other saturated molecules.

It can not be said that the composition of basic ferric sulphate which the pharmacopœia formerly described as  $Fe_4O(SO_4)_8$  (or as  $2Fe_2O_3 \cdot 5SO_3$ ) is explained by saying that it consists of ferric oxide and ferric sulphate united to each other.

Basic salts are also described as salts "containing an excess of the base," or a larger proportion of the base than is contained in the normal salt, or it is said that when only a part of the hydroxyl of a base (a metallic hydroxide) is replaced by an acid-residue a basic salt results; but these statements are as unsatisfactory as the other.

The old formulas commonly employed to represent basic salts are in several cases probably not the true formulas.

Basic salts are in most cases readily shown to be the probable products derived from normal bases (metallic hydroxides) and the common hydroxyl acids, as will be illustrated elsewhere (Chapter XII), just as meta-acids and meta-bases are formed—i. e., by the splitting off of water.

**302.** The following examples will suffice to illustrate the structure of salts:

$NaNO_3$  is sodium nitrate. It is a normal salt, and also a primary salt.

$Na_2SO_4$  is normal sodium sulphate, and a secondary salt.

$NaHSO_4$  is acid sodium sulphate, and a primary salt.

$Na_3C_6H_5O_7$  is normal sodium citrate, or tri-sodium citrate, and a tertiary salt.

$\text{Na}_2\text{HC}_6\text{H}_5\text{O}_7$  is an acid sodium citrate, the di-sodium hydrogen citrate, and a secondary salt.

$\text{NaH}_2\text{C}_6\text{H}_5\text{O}_7$  is another acid sodium citrate, or sodium di-hydrogen citrate, and a primary salt.

$\text{K}_2\text{CO}_3$  is normal potassium carbonate and a secondary salt.

$\text{KHCO}_3$  is acid potassium carbonate, or "potassium acid carbonate," or potassium bicarbonate, and a primary salt.

$\text{K}_2\text{C}_4\text{H}_4\text{O}_6$  is normal potassium tartrate, and a secondary salt.

$\text{KHC}_4\text{H}_4\text{O}_6$  is acid potassium tartrate (cream of tartar), and a primary salt.

$\text{KNaC}_4\text{H}_4\text{O}_6$  is a normal tartrate, the potassium sodium tartrate (Rochelle salt), a secondary salt, and a double-salt.

$\text{Ca}_3(\text{PO}_4)_2$  is normal calcium phosphate, or tri-calcium phosphate, and a tertiary salt.

$\text{CaH}_4(\text{PO}_4)_2$  is an acid calcium phosphate, and a primary salt.

$\text{CaHPO}_4$  is another acid calcium phosphate and a secondary salt.

**303. Sulphur salts** are illustrated by the following comparisons:

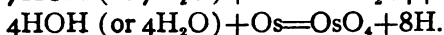
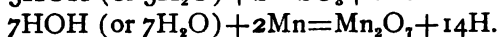
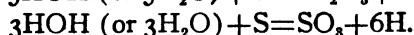
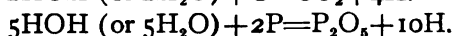
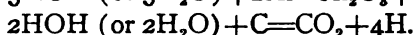
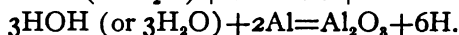
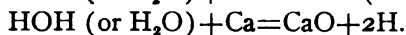
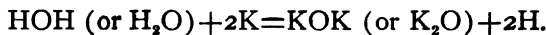
<i>Sulphur Salts.</i>	<i>Oxygen Salts.</i>
$\text{Na}_2\text{SbS}_4$	$\text{Na}_2\text{SbO}_4$
Sodium sulphantimonate.	Sodium antimonate.
$\text{Na}_2\text{HAS}_3$	$\text{Na}_2\text{HASO}_3$
Sodium sulpharsenite.	Sodium arsenite.

Thiosulphates and thionates are salts in which the oxygen is in part or entirely replaced by negative sulphur. The thiosulphates contain both acidic sulphur and negative sulphur, and may or may not contain oxygen. Thionates always contain oxygen as well as sulphur. Sodium thiohyposulphite is  $\text{Na}_2\text{SS}_2$ , corresponding to sodium hyposulphite,  $\text{Na}_2\text{SO}_2$ . Sodium thiosulphate is  $\text{Na}_2\text{SO}_3\text{S}$ , corresponding to sodium sulphate,  $\text{Na}_2\text{SO}_4$ . Sodium tetrathiosulphate is  $\text{Na}_2\text{SS}_4$ . Sodium tetrathionate is  $\text{Na}_2\text{S}_4\text{O}_6$ . Sodium thiocarbonate is  $\text{Na}_2\text{CS}_3$ , corresponding to sodium carbonate.

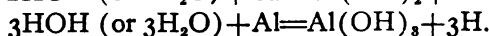
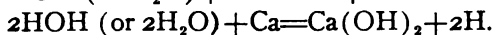
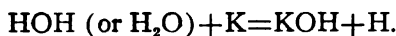
[The nomenclature of these compounds will be understood from the fact that "thio-" is derived from the Greek *theion*, which means sulphur.]

STRUCTURE OF TYPICAL CHEMICAL COMPOUNDS COMPARED WITH  
THE STRUCTURE OF THE WATER MOLECULE.

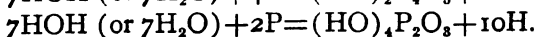
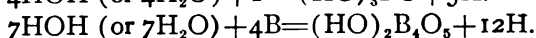
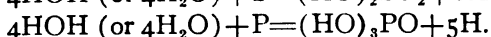
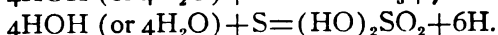
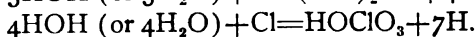
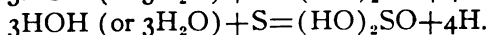
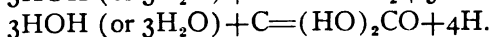
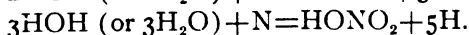
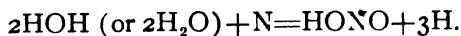
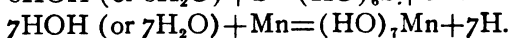
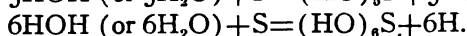
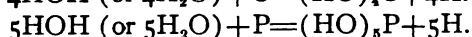
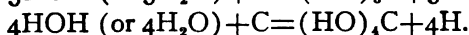
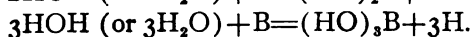
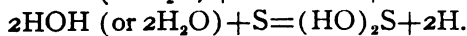
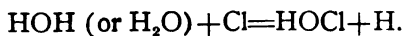
*Oxides.*



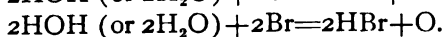
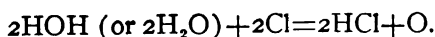
*Hydroxides (Bases).*

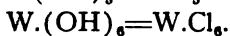
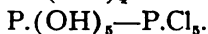
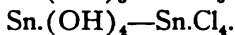
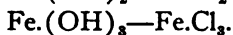
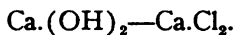
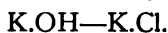
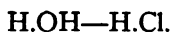
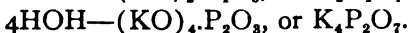
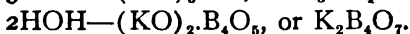
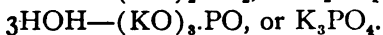
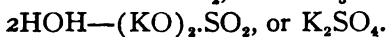
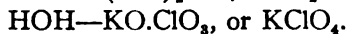
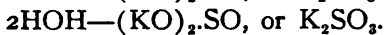
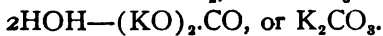
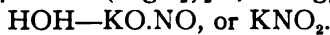
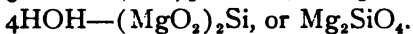
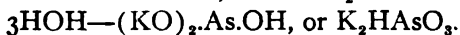
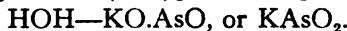
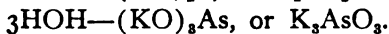
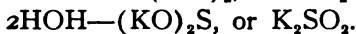
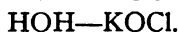
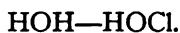


*Acidic Hydroxides (Acids).*



*Hydrogen Acids.*



*Halides in General.**Oxygen Salts.*

## CHAPTER XV.

### THE RELATION OF OXIDES, BASES, ACIDS AND SALTS TO EACH OTHER.

**304.** The **basic** metallic oxides form, with water, basic hydroxides (hydroxides having basic functions) or bases.

The most strongly basic oxides are those of the alkali metals, and next to the oxides of the alkali metals, in that respect, stand the oxides of the alkaline-earth metals.

Non-metallic elements never form basic oxides.

Metals of low valence usually form basic oxides, and, hence, the basic oxides contain, as a rule, a relatively less proportion of oxygen than is contained in the acidic oxides.

Oxides of the type  $R_2O$  are almost exclusively basic oxides, and those of the type  $RO$  are also almost exclusively basic but less pronouncedly basic than the former.

Metallic oxides of the type  $R_2O_3$  are still generally basic, but form weaker bases, and some oxides of this type (formed by non-metallic elements) are acidic (or acid-forming) oxides.

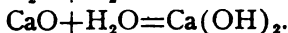
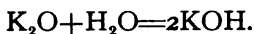
Oxides of the type  $RO_2$  are rarely basic. But they are also rarely acid-formers, or are only feebly acidic.

Basic oxides of the type  $R_2O_3$  are rare and extremely feebly basic, and those of the type  $RO_3$  are still more rare and feeble.

Elements having high atomic weights form preferably basic oxides; and in each of the two families called the alkali metals and the alkali-earth metals, all of which form exclusively basic oxides, any one of the metals having a higher atomic weight forms an oxide of more powerful basic properties than are possessed by the oxide of any other metal of the same family having a lower atomic weight.

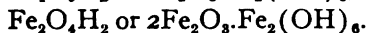
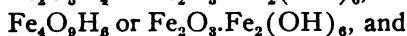
Many of the basic oxides, including all of the oxides of the alkali metals and alkali-earth metals, have a strongly alkaline reaction on moistened litmus paper and form corrosive hydroxides with water.

The formation of bases by the action of water upon basic oxides is shown in the following chemical equations:

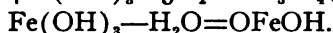
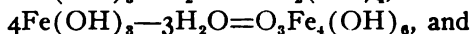


**305.** The formation of meta-bases from basic normal hydroxides by the splitting off of water is well illustrated by the several ferric hydroxides:

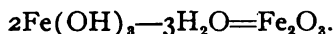
$\text{Fe}(\text{OH})_3$  is normal ferric hydroxide. Three ferric meta-hydroxides are known, which are generally represented as



Their formation and their rational molecular structure may, however, be explained as follows:



When all the hydrogen of any metallic hydroxide is removed, together with half as many oxygen atoms with which the hydrogen combines to form water, the base-forming oxide remains:



**306.** The *acidic* or acid-forming oxides are often called "anhydrides."

Acidic oxides are sometimes metallic oxides, but much more frequently the oxides of non-metallic elements.

Elements having low atomic weights form preferably acidic oxides instead of basic oxides, and acidic oxides, therefore, usually contain a relatively larger proportion of oxygen than the basic oxides.

The most pronounced acidic oxides are generally those of positive tetrads, pentads, hexads and heptads.

Oxides of the highest types,  $\text{RO}_4$  and  $\text{R}_2\text{O}_7$ , are always acidic. The only known oxides of the type  $\text{RO}_4$  are osmic anhydride and ruthenic anhydride. The acid forming oxides of the type  $\text{R}_2\text{O}_7$  include  $\text{Cl}_2\text{O}_7$ ,  $\text{I}_2\text{O}_7$  and  $\text{Mn}_2\text{O}_7$ ; but the  $\text{Cl}_2\text{O}_7$  and  $\text{I}_2\text{O}_7$  have only a theoretical existence, being known only by the salts of their acids.

Oxides of the type  $\text{RO}_3$  are, as a rule, decidedly acidic. Among them are  $\text{SO}_3$ ,  $\text{SeO}_3$ ,  $\text{CrO}_3$  and  $\text{MoO}_3$ .

But several strong acids are formed by anhydrides of the formula  $R_2O_5$ . The acidic oxides of that type include  $N_2O_5$ ,  $P_2O_5$ ,  $As_2O_5$ ,  $Sb_2O_5$ ,  $Cl_2O_5$ ,  $Br_2O_5$ , and  $I_2O_5$ ; but the pentoxides of chlorine and bromine have but a theoretical existence, being represented only by the salts formed by their acids.

Oxides of the type  $RO_2$  are rarely either basic or acidic, but they may form feeble acids.  $SO_2$  and  $CO_2$  are examples of acidic oxides of this type.

Non-metallic oxides of the type  $R_2O_3$  are acidic, and the elements arsenic and antimony also have acidic oxides of this formula.

Acid-forming oxides of the types  $RO$  and  $R_2O$  are very rare.

The acid-forming oxides have an acid reaction on moistened litmus paper because they form acids with water.

**307.** The following examples of acid-forming oxides and the acids representing them will serve to render the relations between acids and anhydrides clear to the student:

$Cl_2O + H_2O$ Hypochlorous oxide.	=	$2HOCl$ , or $HClO$ , Hypochlorous acid (a mono-hydroxyl acid).
$N_2O + H_2O$ "Nitrous oxide."	=	$2HON$ , or $HNO$ , Hyponitrous acid (a mono-hydroxyl acid).
$Cl_2O_3 + H_2O$ Chlorine trioxide.	=	$2HOClO$ , or $HClO_2$ , Chlorous acid (a mono-hydroxyl acid).
$N_2O_3 + H_2O$ Nitrogen trioxide.	=	$2HONO$ , or $HNO_2$ , Nitrous acid (a mono-hydroxyl acid).
$SO_2 + H_2O$ Sulphur dioxide.	=	$(HO)_2SO$ , or $H_2SO_3$ , Sulphurous acid (a di-hydroxyl acid).
$CO_2 + H_2O$ Carbon dioxide.	=	$(HO)_2CO$ , or $H_2CO_3$ , Carbonic acid (a di-hydroxyl acid).
$As_2O_3 + 3H_2O$ Arsenous oxide.	=	$2(HO)_2AsHO$ , or $H_2AsHO_3$ , Arsenous acid.
$N_2O_5 + H_2O$ Nitrogen pentoxide.	=	$2HONO_2$ , or $HNO_3$ , Nitric acid (a mono-hydroxyl acid).
$P_2O_5 + 3H_2O$ Phosphorus pentoxide.	=	$2(HO)_3PO$ , or $H_3PO_4$ , Phosphoric acid (a tri-hydroxyl acid).
$SO_3 + H_2O$ Sulphur trioxide.	=	$(HO)_2SO_2$ , or $H_2SO_4$ , Sulphuric acid (a di-hydroxyl acid).

**308.** The **normal acids**,\* known by their salts or otherwise, are few in number.

Theoretically an element of variable valence can have more than one normal acid, for it can have one such acid for each degree of its positive valence, as represented in the following table:

ClOH is the normal acid of univalent chlorine.  
 $\text{Cl}(\text{OH})_3$  is the normal acid of trivalent chlorine.  
 $\text{Cl}(\text{OH})_5$  is the normal acid of quinquivalent chlorine.  
 $\text{Cl}(\text{OH})_7$  is the normal acid of septivalent chlorine.  
 $\text{Br}(\text{OH})_5$  is the normal acid of quinquivalent bromine.  
 $\text{I}(\text{OH})_5$  is the normal acid of quinquivalent iodine.  
 $\text{I}(\text{OH})_7$  is the normal acid of septivalent iodine.  
 $\text{N}(\text{OH})_3$  is the normal acid of trivalent nitrogen.  
 $\text{N}(\text{OH})_5$  is the normal acid of quinquivalent nitrogen.  
 $\text{P}(\text{OH})_5$  is the normal acid of quinquivalent phosphorus.  
 $\text{B}(\text{OH})_3$  is the normal acid of trivalent boron.  
 $\text{S}(\text{OH})_4$  is the normal acid of quadrivalent sulphur.  
 $\text{S}(\text{OH})_6$  is the normal acid of sexivalent sulphur.  
 $\text{C}(\text{OH})_4$  is the normal acid of quadrivalent carbon.  
 $\text{Si}(\text{OH})_4$  is the normal acid of quadrivalent silicon.

Acids containing one hydroxyl group are mono-hydroxyl acids; those containing two hydroxyls are di-hydroxyl acids; those having three are tri-hydroxyl acids; tetra-hydroxyl acids contain four hydroxyls; penta-hydroxyl acids contain five; hexa-hydroxyl acids six, and hepta-hydroxyl acids contain seven hydroxyls.

Boric acid,  $\text{H}_3\text{BO}_3$ , is a well known and stable compound. The hypochlorites of potassium, sodium and calcium are well known salts of HClO. Antimonous acid and arsenous acid exist. Salts of normal carbonic acid,  $\text{H}_2\text{CO}_3$ , are known to organic chemistry and mineralogy. Kaolin,  $\text{AlHSiO}_4$ , is a common normal silicate.

When common sulphuric acid,  $\text{H}_2\text{SO}_4$ , is mixed with water a violent chemical reaction ensues which is evidenced by the excitation of great thermal energy. If the acid be absolute

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\* Some writers call the normal acids "ortho-acids," defining them as "acids in which all the oxygen performs a linking function."

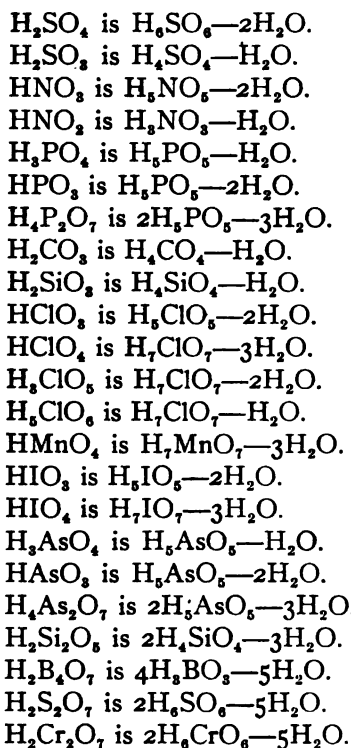
$\text{H}_2\text{SO}_4$ , and the proportions the exact quantities required by the molecular weights, the reactions are those represented by the following equations:  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} = \text{H}_4\text{SO}_6$ ; and, when another molecule of water is added,  $\text{H}_4\text{SO}_6 + \text{H}_2\text{O} = \text{H}_6\text{SO}_8$ . The acid  $\text{H}_4\text{SO}_6$  is crystallizable and, when it is mixed with water, it reacts with it, causing very great evolution of heat-motion as it forms the normal sulphuric acid,  $\text{H}_6\text{SO}_8$ . The normal sulphuric acid is commonly supposed to be an acid containing about 73.134 per cent of  $\text{H}_2\text{SO}_4$  and 26.866 per cent of water; the  $\text{H}_4\text{SO}_6$  is commonly regarded as composed of 84.483 per cent of  $\text{H}_2\text{SO}_4$  and 15.517 per cent of water.

The pharmacopoeial nitric acid is described as "a liquid composed of 68 per cent by weight of absolute nitric acid,  $\text{HNO}_3$ , and 32 per cent of water," and has the sp. w. 1.414. The boiling point of this acid is constant, and a stronger acid loses strength by heating, while a weaker acid loses water, so that in the distillation of nitric acid the constant product is one corresponding to 68 per cent of  $\text{HNO}_3$ . Normal nitric acid is  $\text{H}_3\text{NO}_6$ , corresponding to  $\text{HNO}_3 + 2\text{H}_2\text{O}$ , or a nitric acid containing about 63.6 per cent of  $\text{HNO}_3$ . But it is highly probable that the constant boiling point of a nitric acid of 68 per cent strength depends primarily upon the fact that it consists chiefly of  $\text{H}_3\text{NO}_6$ .

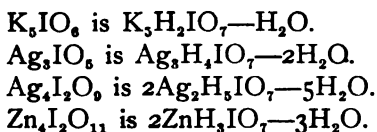
Finally, the formation of meta-acids and their salts, the composition of which remains unexplained except upon the theory of their derivation from the corresponding normal acids and their salts, strongly suggests the existence of saturated hydroxyl compounds (or normal acids) of the acid-forming elements.

**309. Meta-acids** are the hydroxyl acids formed by the separation or subtraction of one or more molecules of water from one or more molecules of the *normal acids*. These meta-acids may be termed *primary meta-acids* to distinguish them from the *secondary meta-acids*, which are derived from the primary meta-acids in the same manner in which the latter are derived from the normal acids.

The most common inorganic acids are meta-acids, and their relations to the normal acids from which they are derived are shown in this exhibit, which also includes several less common and less stable meta-acids:



Among the salts of meta-acids are the common sulphates and sulphites, nitrates and nitrites, phosphates, metaphosphates, pyrophosphates, carbonates, silicates, chlorates, perchlorates, iodates, per-iodates, arsenates, arsenites, antimonates, antimonites, pyroarsenates, pyroantimonates, disilicates, tetraborates, and pyrosulphates.



$\text{KIO}_4$  is potassium tri-meta-periodate;  $\text{K}_5\text{IO}_6$  is a salt of mono-meta-per-iodic acid,  $\text{H}_5\text{IO}_5$ , which is  $\text{H}_7\text{IO}_7 - \text{H}_2\text{O}$ ;  $\text{Ag}_3\text{IO}_5$  is a salt of di-meta-per-iodic acid,  $\text{H}_3\text{IO}_3$ , which is  $\text{H}_7\text{IO}_7 - 2\text{H}_2\text{O}$ ;  $\text{Ag}_4\text{I}_2\text{O}_9$  is a salt of  $\text{H}_4\text{I}_2\text{O}_9$  formed by the splitting off of one

molecule of water from two molecules of di-meta-per-iodic acid ( $2\text{H}_5\text{IO}_6 - \text{H}_2\text{O} = \text{H}_4\text{I}_2\text{O}_9$ ); and  $\text{Zn}_4\text{I}_2\text{O}_{11}$  is a salt of  $\text{H}_8\text{I}_2\text{O}_{11}$  formed when one molecule of water splits off from two molecules of mono-meta-per-iodic acid ( $2\text{H}_5\text{IO}_6 - \text{H}_2\text{O} = \text{H}_8\text{I}_2\text{O}_{11}$ ).

It will be seen that the so-called "orthocarbonic acid,"  $\text{H}_4\text{CO}_4$ , and "ortho-silicic acid,"  $\text{H}_4\text{SiO}_4$ , are the normal hydroxyl acids of carbon and silicon; but the common phosphoric acid,  $\text{H}_3\text{PO}_4$ , generally called "ortho-phosphoric acid," is in fact the mono-meta-phosphoric acid, while the acid commonly called "meta-phosphoric acid," which, in commerce, goes by the name of *glacial phosphoric acid*, is di-meta-phosphoric acid.

**310.** A *mono-meta-acid* is an acid derived from the normal acid by the subtraction of *one* molecule of water; when *two* molecules of water are split off from one molecule of the normal acid a *di-meta-acid* is the result; the removal of *three* molecules of water from one molecule of normal acid leaves the *tri-meta-acid*.

**311.** If the molecular formula of any mono-basic or tribasic hydroxyl acid be doubled it can then be split up into water and the acid-forming oxide corresponding to that acid. ✓

If the number of hydrogen atoms in the molecular formula of an inorganic hydroxyl acid be an even number, then the corresponding acid-forming oxide will remain after deducting as many molecules of water as half the number of hydrogen atoms.

This rule holds good in regard to all normal acids and their derived meta-acids. Hence when all of the hydrogen of such an acid is removed together with half as many atoms of oxygen (with which the hydrogen unites to form water), the acidic oxide or anhydride remains.

[But this is not the case with acids *not* derived from the normal acids or formed from anhydrides with water. An example of this kind is hypophosphorus acid,  $\text{HOPH}_2\text{O}$ , which contains two hydrogen atoms united directly to the acidic element, the phosphorus.]

**312.** The basicity of any inorganic hydroxyl acid containing four oxygen atoms is necessarily expressed by the number representing the number of hydrogen atoms with which the acid-forming element forms a binary compound when it exercises negative polarity. Thus:

$\text{HClO}_4$  is monobasic because the hydrogen compound of Cl is  $\text{HCl}$ .

$\text{H}_2\text{SO}_4$  is bibasic because the hydrogen compound of S is  $\text{H}_2\text{S}$ .

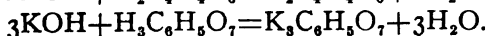
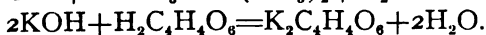
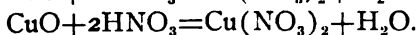
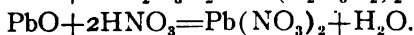
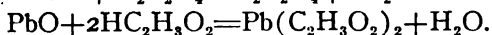
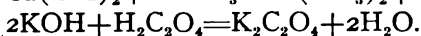
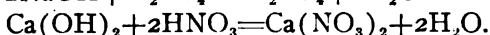
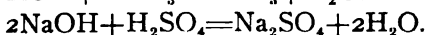
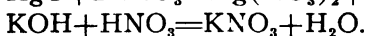
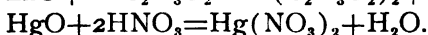
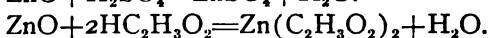
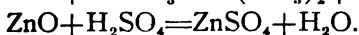
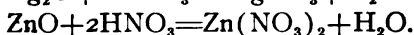
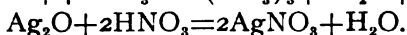
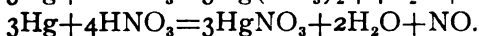
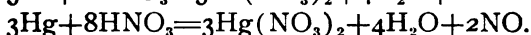
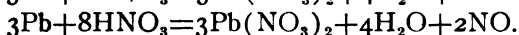
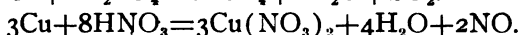
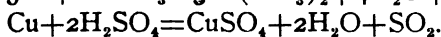
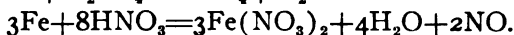
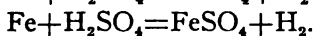
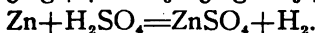
$\text{H}_3\text{PO}_4$  is tribasic because the hydrogen compound of P is  $\text{H}_3\text{P}$ .

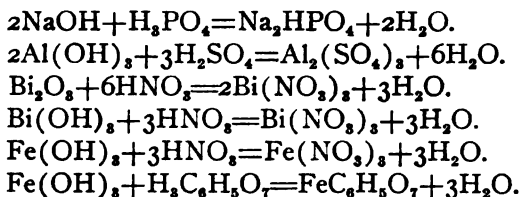
$\text{H}_4\text{SiO}_4$  is tetrabasic because the hydrogen compound of Si is  $\text{H}_4\text{Si}$ .

**313. Acid-forming metals.** Molybdenum, tungsten, chromium, manganese, arsenic, antimony, bismuth, tin and tellurium, which have the physical properties of metals, nevertheless exercise acidic functions.

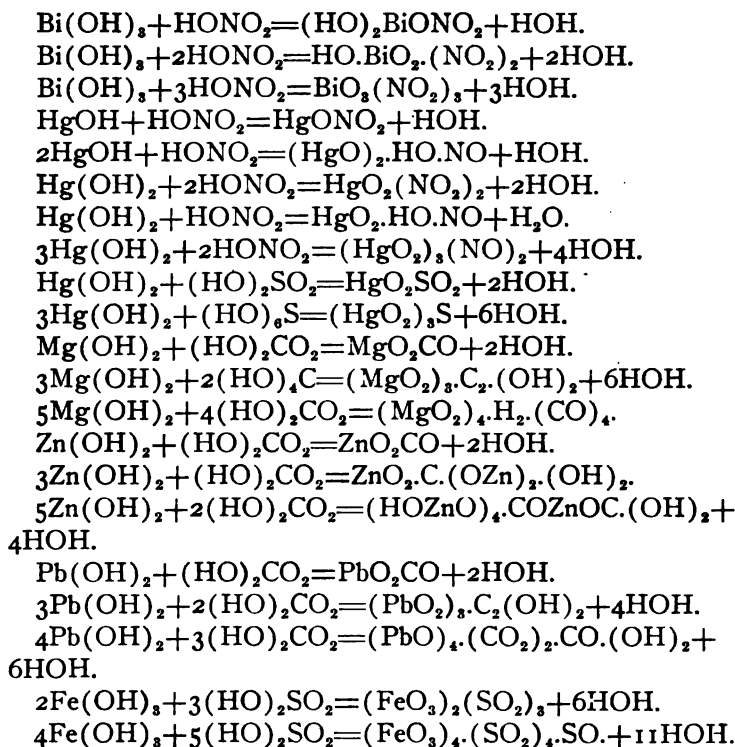
Aluminates, zincates, ferrates, plumbates, are also known.

**314.** The formation of **salts** by acids with the metals and with metallic oxides and hydroxides is sufficiently illustrated by the following examples:





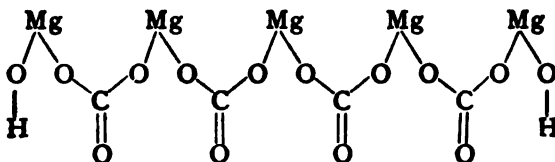
**315.** The formation of *basic salts* from acids and bases is illustrated by the following comparisons with the formation of the normal salts:



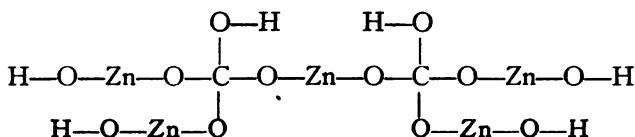
**316.** The common magnesium carbonate, instead of being  $(\text{MgCO}_3)_4.\text{Mg}(\text{OH})_2$ , might be represented as



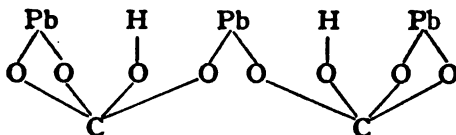
Its structural bonds are accounted for as follows:



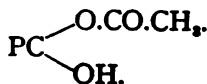
Common zinc carbonate, generally written  $(\text{ZnCO}_3)_2 \cdot 3\text{Zn}(\text{OH})_2$ , may be represented as



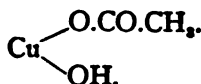
The most common lead carbonate is usually written  $(\text{PbCO}_3)_2 \cdot \text{Pb}(\text{OH})_2$ , but it is probably a salt derived from normal carbonic acid,  $(\text{HO})_4\text{C}$ , and, if so, may be represented by  $\text{Pb}_3\text{H}_2(\text{CO}_4)_2$ , or



The subacetate of lead of the officinal solution is generally represented by the formula  $\text{PbO} \cdot \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , or by  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Pb}(\text{OH})_2$ ; but it may be more rationally considered as

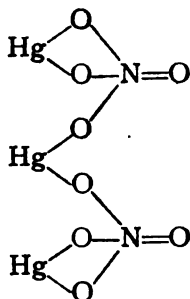


Basic copper acetate is

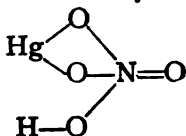


Yellow basic mercuric sulphate (or sub-sulphate) is commonly represented as  $(\text{HgO})_2 \cdot \text{HgSO}_4$ ; but it might rationally be assumed to be the mercuric salt of  $(\text{HO})_6\text{S}$ , and written  $(\text{HgO}_2)_2 \cdot \text{S}$ .

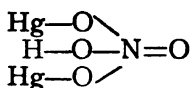
One of the basic nitrates of mercury which is commonly written  $(\text{HgO})_2.\text{Hg}(\text{NO}_3)_2$ , is rather  $(\text{HgO}_2)_3(\text{NO})_2$ , or



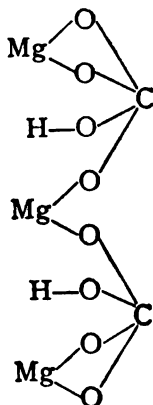
Another is



One of the basic mercurous nitrates is

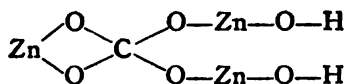


One magnesium carbonate represented as  $\text{Mg}(\text{OH})_2.2\text{MgCO}_3$  is probably:

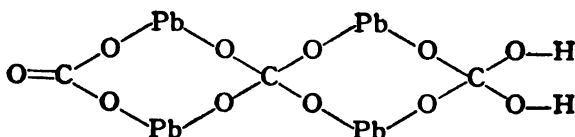


and hence derived from  $(\text{HO})_4\text{C}$ .

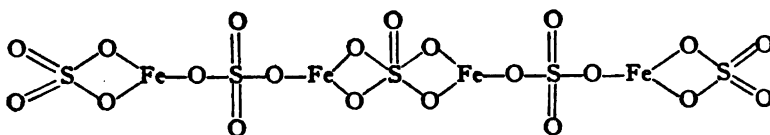
There is a zinc carbonate of the composition



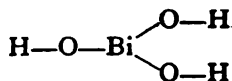
A lead carbonate is known which is probably:



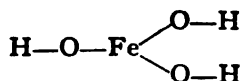
The basic ferric sulphate contained in the solution of subsulphate of iron of the Pharmacopœia, and which has been represented as  $\text{Fe}_2\text{O}_3 \cdot 5\text{Fe}_2(\text{SO}_4)_3$ , or as  $\text{Fe}_4\text{O}(\text{SO}_4)_5$ , may be pictured as:



**317.** When water is split off from a basic hydroxide it follows that the *basic element* becomes combined with one oxygen atom for each pair of hydroxyls lost; and when water is split off from an acidic hydroxide it follows that the *acidic element* becomes combined with one oxygen atom for each pair of hydroxyls lost (or for each molecule of water split off).

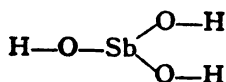


thus becomes  $\text{OBiOH}$ , called bismuthyl hydroxide;

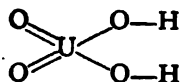


becomes  $\text{OFeOH}$ , which may be called ferryl hydroxide;

OSbCl called antimonyl chloride, may be supposed to be derived from



uranyl hydroxide,



may be supposed to correspond to normal uranium hydroxide,  $\text{U}(\text{OH})_6$  which does not exist;  $\text{HONO}$  is nitrosyl hydroxide, while  $\text{HONO}_2$  is nitryl hydroxide;  $(\text{HO})_2\text{CO}$  is carbonyl hydroxide;  $(\text{HO})_2\text{SO}_2$  is sulphuryl hydroxide;  $(\text{HO})_2\text{SO}$  is sulphurosyl hydroxide; potassium aurate,  $\text{KOAuO}$ , is derived from auric hydroxide,  $\text{Au}(\text{OH})_3$ .

**318.** When metallic hydroxides form salts with the hydroxyl acids the reactions may be represented in two different ways:

1.  $\text{KOH} + \text{HONO}_2 = \text{KONO}_2 + \text{HOH}$ .
2.  $\text{KOH} + \text{HNO}_3 = \text{KNO}_3 + \text{HOH}$ .

We can assume that the  $\text{KOH}$  has exchanged its  $\text{H}$  for  $\text{NO}_2$ , or its  $\text{OH}$  for  $\text{NO}_3$ ; or that  $\text{HONO}_2$  has exchanged its  $\text{HO}$  for  $\text{KO}$ , or that  $\text{HNO}_3$  has exchanged its  $\text{H}$  for  $\text{K}$ . Yet, in each case the net result is that the  $\text{H}$  of the acid and the metal of the base exchange places, and that the products are salt and water.

Normal salts formed by strong acids with strong bases have generally a neutral **reaction on test paper**. But normal salts formed by strong bases with weak acids often have an alkaline reaction, while those formed by feeble bases with strong acids have an acid reaction.

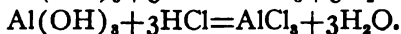
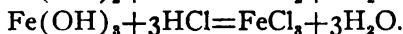
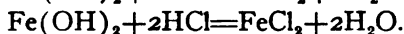
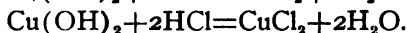
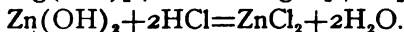
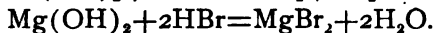
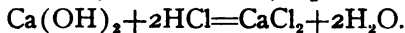
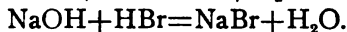
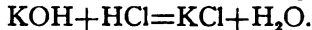
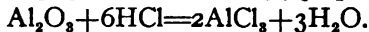
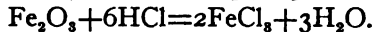
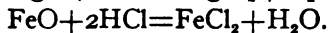
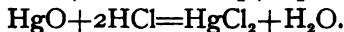
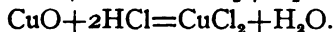
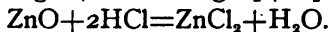
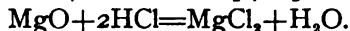
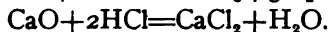
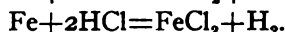
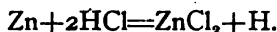
*Normal* sodium sulphate has a neutral reaction on litmus paper, for it does not turn blue litmus red nor red litmus blue; but *acid* sodium sulphate has an acid reaction, turning blue litmus red.

Acid potassium carbonate and normal potassium carbonate both have an alkaline reaction because potassium is the most powerful

of all the common basic elements while the carbonate radical is a very feeble acid-radical.

The solution of subsulphate of iron of the Pharmacopœia, although a basic salt, has nevertheless an acid reaction because iron is comparatively not strongly basic, while the sulphate radical is a powerful acidic radical.

**319.** The formation of **halides** by the hydrogen acids with metals and with the metallic oxides and hydroxides is illustrated by the following examples:



## CHAPTER XVI.

### STRUCTURE OF THE METALLIC OXYGEN SALTS OF THE COMMON ACIDS.

**320.** The **Hypochlorites** are the salts of the normal acid HOCl.

KOCl, or KClO is potassium hypochlorite.

NaOCl, or NaClO is sodium hypochlorite.

CaO<sub>2</sub>Cl<sub>2</sub>, or Ca(ClO)<sub>2</sub> is calcium hypochlorite.

**321.** **Chlorates** are the salts of di-meta-chloric-acid, HOClO<sub>2</sub>, or HClO<sub>3</sub>. Their structure is shown in

KOCIO<sub>2</sub>, or KClO<sub>3</sub>, potassium chlorate.

NaOCIO<sub>2</sub>, or NaClO<sub>3</sub>, sodium chlorate.

LiOCIO<sub>2</sub>, or LiClO<sub>3</sub>, lithium chlorate.

SrO<sub>2</sub>(ClO<sub>2</sub>)<sub>2</sub>, or Sr(ClO<sub>3</sub>)<sub>2</sub>, strontium chlorate.

CaO<sub>2</sub>(ClO<sub>2</sub>)<sub>2</sub>, or Ca(ClO<sub>3</sub>)<sub>2</sub>, calcium chlorate.

**322.** **Sulphites** are formed by mono-meta-sulphurous acid, (HO)<sub>2</sub>SO, or H<sub>2</sub>SO<sub>3</sub>.

The following are common sulphites:

(HO)<sub>2</sub>SO, or H<sub>2</sub>SO<sub>3</sub>, hydrogen sulphite, or sulphurous acid.

(NaO)<sub>2</sub>SO, or Na<sub>2</sub>SO<sub>3</sub>.7H<sub>2</sub>O, sodium sulphite.

CaO<sub>2</sub>SO, or CaSO<sub>3</sub>.2H<sub>2</sub>O, calcium sulphite.

MgO<sub>2</sub>SO, or MgSO<sub>3</sub>.6H<sub>2</sub>O, magnesium sulphite.

**323.** **Sulphates** may be of at least two kinds. The most common sulphates are those of the di-meta-sulphuric acid, (HO)<sub>2</sub>SO<sub>2</sub>, or H<sub>2</sub>SO<sub>4</sub>; but salts of mono-meta-sulphuric acid, (HO)<sub>4</sub>SO, or H<sub>4</sub>SO<sub>6</sub> are also known.

Their structure is shown in the following examples of common sulphates:

(HO)<sub>2</sub>SO<sub>2</sub>, or H<sub>2</sub>SO<sub>4</sub>, hydrogen di-meta-sulphate, or common sulphuric acid.

(KO)<sub>2</sub>SO<sub>2</sub>, or K<sub>2</sub>SO<sub>4</sub>, common normal potassium sulphate.

KOHOSO<sub>2</sub>, or KHSO<sub>4</sub>, acid potassium sulphate, or potassium bisulphate.

$(\text{NaO})_2\text{SO}_2$ , or  $\text{Na}_2\text{SO}_4$ , sodium sulphate.  
 $(\text{NaO})_2\text{SO}_2 \cdot 10\text{H}_2\text{O}$ , crystallized sodium sulphate.  
 $\text{NaOHOSO}_2$ , or  $\text{NaHSO}_4$ , sodium bisulphate.  
 $(\text{H}_4\text{NO})_2\text{SO}_2$ , or  $(\text{H}_4\text{N})_2\text{SO}_4$ , ammonium sulphate.  
 $\text{CaO}_2\text{SO}_2$ , or  $\text{CaSO}_4$ , anhydrous calcium sulphate.  
 $\text{CaO}_2 \cdot \text{SO}_2 \cdot 2\text{H}_2\text{O}$ , or  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , calcium sulphate with water.

$\text{MnO}_2\text{SO}_2 \cdot 7\text{H}_2\text{O}$ , or  $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ , manganous sulphate.  
 $\text{CuO}_2\text{SO}_2 \cdot 5\text{H}_2\text{O}$ , or  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , cupric sulphate.  
 $\text{HgO}_2\text{SO}_2$ , or  $\text{HgSO}_4$ , mercuric sulphate.  
 $(\text{AlO}_3)_2(\text{SO}_2)_3$ , or  $\text{Al}_2(\text{SO}_4)_3$ , aluminum sulphate.  
 $\text{AlO}_3\text{KO}(\text{SO}_2)_2$ , or  $\text{AlK}(\text{SO}_4)_2$ , dried alum.  
 $\text{AlO}_3\text{KO}(\text{SO}_2)_2 \cdot 12\text{H}_2\text{O}$ , or  $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , alum.  
 $\text{AlO}_3\text{H}_4\text{NO}(\text{SO}_2)_2 \cdot 12\text{H}_2\text{O}$ , or  $\text{AlH}_4\text{N}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , ammonium alum.  
 $\text{FeO}_3\text{H}_4\text{NO}(\text{SO}_2)_2 \cdot 12\text{H}_2\text{O}$ , or  $\text{FeH}_4\text{N}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , ammonio-ferric alum.  
 $(\text{FeO}_3)_2(\text{SO}_2)_3$ , or  $\text{Fe}_2(\text{SO}_4)_3$ , ferric sulphate.  
 $(\text{FeO}_3)_4\text{SO}(\text{SO}_2)_4$ , or  $\text{Fe}_4\text{O}(\text{SO}_4)_6$ , basic ferric sulphate.  
 $\text{HgO}_2(\text{HgO})_2\text{SO}_2$ , basic mercuric sulphate.

$\text{MgO}_2(\text{HO})_2\text{SO}$ , or  $\text{MgH}_2\text{SO}_5$ , magnesium mono-meta-sulphate, or dried Epsom salt.

$\text{MgO}_2(\text{HO})_2\text{SO} \cdot 6\text{H}_2\text{O}$ , or  $\text{MgH}_2\text{SO}_5 \cdot 6\text{H}_2\text{O}$ , Epsom salt.  
 $\text{ZnO}_2(\text{HO})_2\text{SO}$ , or  $\text{ZnH}_2\text{SO}_5$ , dried zinc sulphate.  
 $\text{ZnO}_2(\text{HO})_2\text{SO} \cdot 6\text{H}_2\text{O}$ , or  $\text{ZnH}_2\text{SO}_5 \cdot 6\text{H}_2\text{O}$ , crystallized zinc sulphate.

$\text{FeO}_2(\text{HO})_2\text{SO}$ , or  $\text{FeH}_2\text{SO}_5$ , dried ferrous sulphate.  
 $\text{FeO}_2(\text{HO})_2\text{SO} \cdot 6\text{H}_2\text{O}$ , or  $\text{FeH}_2\text{SO}_5 \cdot 6\text{H}_2\text{O}$ , crystallized ferrous sulphate.

**324. Thiosulphates.** Thiosulphuric acid is  $(\text{HO})_2\text{SOS}$ , or  $\text{HO} \cdot \text{SO}_2 \cdot \text{SH}$ , or a sulphuric acid in which one of the atoms of oxygen has been exchanged for sulphur. Sodium thiosulphate is commonly called sodium hyposulphite; but hyposulphurous acid is  $(\text{HO})_2\text{S}$ , or  $\text{H}_2\text{SO}_2$ .

$\text{Na}_2\text{S}_2\text{O}_3$ , is sodium thiosulphate.

$\text{CaS}_2\text{O}_3$ , is calcium thiosulphate.

**325. Nitrites** are formed by nitrous acid,  $\text{HONO}$ , or  $\text{HNO}_2$ . This is a mono-meta-acid.

Sodium nitrite is  $\text{NaO}\cdot\text{NO}$ , or  $\text{NaNO}_2$ .

**326. Nitrates** are the salts of nitric acid,  $\text{HONO}_2$ , or  $\text{HNO}_3$ , which is a di-meta-acid.

The structure of nitrates is shown in the following table:

$\text{HONO}_2$ , or  $\text{HNO}_3$ , hydrogen nitrate, or nitric acid.

$\text{KONO}_2$ , or  $\text{KNO}_3$ , potassium nitrate.

$\text{NaONO}_2$ , or  $\text{NaNO}_3$ , sodium nitrate.

$\text{H}_4\text{NONO}_2$ , or  $\text{H}_4\text{NNO}_3$ , ammonium nitrate.

$\text{AgONO}_2$ , or  $\text{AgNO}_3$ , silver nitrate.

$\text{OBiONO}_2$ , or  $\text{OBiNO}_3$ , bismuthyl nitrate.

$\text{OBiONO}_2\cdot\text{H}_2\text{O}$ , or  $\text{OBiNO}_3\cdot\text{H}_2\text{O}$ , the ordinary "subnitrate of bismuth."

$\text{BaO}_2(\text{NO}_2)_2$ , or  $\text{Ba}(\text{NO}_3)_2$ , barium nitrate.

$\text{SrO}_2(\text{NO}_2)_2$ , or  $\text{Sr}(\text{NO}_3)_2$ , strontium nitrate.

$\text{PbO}_2(\text{NO}_2)_2$ , or  $\text{Pb}(\text{NO}_3)_2$ , lead nitrate.

$\text{CuO}_2(\text{NO}_2)_2$ , or  $\text{Cu}(\text{NO}_3)_2$ , copper nitrate.

$\text{HgO}_2(\text{NO}_2)_2$ , or  $\text{Hg}(\text{NO}_3)_2$ , mercuric nitrate.

$\text{HgONO}_2$ , or  $\text{HgNO}_3$ , mercurous nitrate.

$\text{BiO}_3(\text{NO}_2)_3$ , or  $\text{Bi}(\text{NO}_3)_3$ , bismuth nitrate.

$\text{FeO}_3(\text{NO}_2)_3$ , or  $\text{Fe}(\text{NO}_3)_3$ , ferric nitrate.

**327. Hypophosphites** are the salts of the peculiar acid  $\text{HOPH}_2\text{O}$ , or  $\text{HPH}_2\text{O}_2$ , called hypophosphorous acid, in which the acidic element, P, has a valence of 5 but a polarity-value of +1. Two of the hydrogen atoms of the molecule are united directly to the phosphorus. It is the only inorganic hydroxyl acid known which contains a greater number of hydrogen atoms than of oxygen atoms. It is monobasic.

$\text{HOPH}_2\text{O}$ , or  $\text{HPH}_2\text{O}_2$ , hydrogen hypophosphite or hypophosphorous acid.

$\text{KOPH}_2\text{O}$ , or  $\text{KPH}_2\text{O}_2$ , potassium hypophosphite.

$\text{NaOPH}_2\text{O}$ , or  $\text{NaPH}_2\text{O}_2$ , sodium hypophosphite.

$\text{CaO}_2(\text{PH}_2\text{O})_2$ , or  $\text{Ca}(\text{PH}_2\text{O}_2)_2$ , calcium hypophosphite.

$\text{FeO}_2(\text{PH}_2\text{O})_2$ , or  $\text{Fe}(\text{PH}_2\text{O}_2)_2$ , calcium hypophosphite.

$\text{FeO}_3(\text{PH}_2\text{O})_3$ , or  $\text{Fe}(\text{PH}_2\text{O}_2)_3$ , ferric hypophosphite.

**328. Phosphates.** The common "phosphates," which are commonly called "ortho-phosphates," are the salts of mono-meta-phosphoric acid,  $(\text{HO})_3\text{PO}$ , or  $\text{H}_3\text{PO}_4$ .

The most important "phosphates" include the following:

$(\text{HO})_3\text{PO}$ , or  $\text{H}_3\text{PO}_4$ , hydrogen mono-meta-phosphate, or ordinary phosphoric acid.

$(\text{KO})_2\cdot\text{HO}\cdot\text{PO}$ , or  $\text{K}_2\text{HPO}_4$ , potassium phosphate.

$(\text{NaO})_2\cdot\text{HO}\cdot\text{PO}$ , or  $\text{Na}_2\text{HPO}_4$ , sodium phosphate.

$\text{NaO}\cdot\text{H}_4\text{NO}\cdot\text{HO}\cdot\text{PO}\cdot 4\text{H}_2\text{O}$ , or  $\text{NaH}_4\text{NHPO}_4\cdot 4\text{H}_2\text{O}$ , sodium-ammonium-hydrogen phosphate, or "microcosmic salt."

$(\text{H}_4\text{NO})_2\cdot\text{HO}\cdot\text{PO}$ , or  $(\text{H}_4\text{N})_2\text{HPO}_4$ , ammonium phosphate.

$(\text{CaO}_2)_3(\text{PO})_2$ , or  $\text{Ca}_3(\text{PO}_4)_2$ , tri-calcium phosphate.

$\text{CaO}_2\cdot\text{HO}\cdot\text{PO}$ , or  $\text{CaHPO}_4$ , calcium-hydrogen phosphate.

$\text{CaO}_2\cdot(\text{HO})_4\cdot(\text{PO})_2$ , or  $\text{CaH}_4(\text{PO}_4)_2$ , acid calcium phosphate.

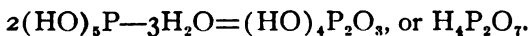
$\text{FeO}_3\text{PO}\cdot 2\text{H}_2\text{O}$ , or  $\text{FePO}_4\cdot 2\text{H}_2\text{O}$ , ferric phosphate.

$(\text{FeO}_2)_3(\text{PO})_2\cdot 8\text{H}_2\text{O}$ , or  $\text{Fe}_3(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}$ , ferrous phosphate.

**329. Metaphosphates.** The ice-like "glacial phosphoric acid" is generally called "meta-phosphoric acid." It is a di-meta-acid, its molecular formula being  $\text{HOPO}_2$ , or  $\text{HPO}_3$ .

Ferric di-metaphosphate is  $\text{FeO}_3(\text{PO}_2)_3$ . No other metaphosphate possesses special interest.

**330. Pyrophosphates** are the salts formed by pyrophosphoric acid which is a meta-acid obtained by the abstraction of three molecules of water from a double molecule of normal phosphoric acid:



Sodium pyrophosphate is  $(\text{NaO})_4\text{P}_2\text{O}_7$ , or  $\text{Na}_4\text{P}_2\text{O}_7$ .

Ferric pyrophosphate is  $(\text{FeO}_3)_4(\text{P}_2\text{O}_7)_3$ , or  $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ .

**331. Arsenites.** When arsenous oxide,  $\text{As}_4\text{O}_6$  (commonly written  $\text{As}_2\text{O}_3$ ) is dissolved in water arsenous acid,  $(\text{HO})_2\text{AsHO}$ , or  $\text{H}_2\text{AsHO}_3$ , is formed, instead of  $(\text{HO})_3\text{As}$ , as might be expected. It will be seen that the polarity-value of the As is +3 both in  $(\text{HO})_3\text{As}$  and in  $(\text{HO})_2\text{AsHO}$ ; but the valence of the As is 3 in  $(\text{HO})_3\text{As}$  while it is 5 in  $(\text{HO})_2\text{AsHO}$ . The third hydrogen atom is directly united to the As and not to the oxygen. Hence the acid is bibasic.

Potassium arsenite is  $(\text{KO})_2\text{AsHO}$ , or  $\text{K}_2\text{AsHO}_3$ .

Sodium arsenite is  $(\text{NaO})_2\text{AsHO}$ , or  $\text{Na}_2\text{AsHO}_3$ .

**332. Arsenates** have a molecular structure analogous to that of the common phosphates (the salts of mono-meta-phosphoric acid, generally called "orthophosphates").

$(\text{HO})_3\text{AsO}$ , or  $\text{H}_3\text{AsO}_4$ , hydrogen arsenate or arsenic acid.

$(\text{NaO})_2\text{HOAsO}$ , or  $\text{Na}_2\text{HAsO}_4$ , sodium arsenate, dried.

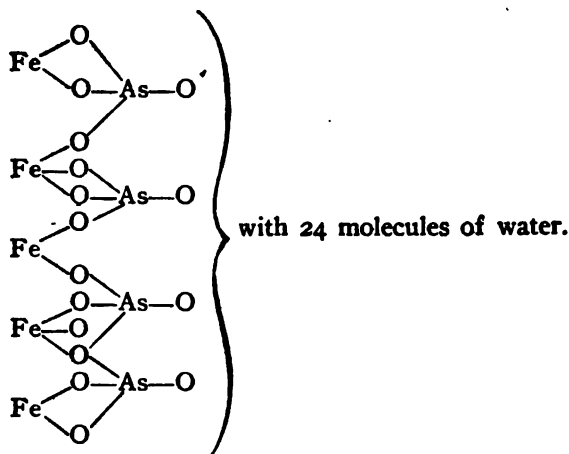
$(\text{NaO})_2\text{HOAsO} \cdot 2\text{H}_2\text{O}$ , effloresced sodium arsenate.

$(\text{NaO})_2\text{HOAsO} \cdot 7\text{H}_2\text{O}$ , crystallized sodium arsenate.

$(\text{FeO}_2)_3(\text{AsO})_2$ , ferrous arsenate.

$\text{FeO}_3\text{AsO}$ , ferric arsenate.

The ferroso-ferric arsenate, commonly written  $\text{Fe}_3(\text{AsO}_4)_2 \cdot \text{Fe}_2(\text{AsO}_4)_2 \cdot 24\text{H}_2\text{O}$ , may be represented as



**333. Pyroarsenates** correspond in structure to the pyrophosphates, and the molecular formula of sodium pyroarsenate is accordingly  $(\text{NaO})_4\text{As}_2\text{O}_8$ , or  $\text{Na}_4\text{As}_2\text{O}_7$ .

**334. Carbonates** are the salts of meta-carbonic acid,  $(\text{HO})_2\text{CO}$ , or  $\text{H}_2\text{CO}_3$ .

$(\text{HO})_2\text{CO}$ , or  $\text{H}_2\text{CO}_3$ , hydrogen carbonate, or carbonic acid.

$(\text{KO})_2\text{CO}$ , or  $\text{K}_2\text{CO}_3$ , potassium carbonate.

$2(\text{KO})_2\text{CO}_2 \cdot 3\text{H}_2\text{O}$ , common potassium carbonate.

$\text{KO} \cdot \text{HO} \cdot \text{CO}$ , or  $\text{KHCO}_3$ , potassium bicarbonate.

$(\text{NaO})_2\text{CO}$ , or  $\text{Na}_2\text{CO}_3$ , sodium carbonate, anhydrous.

$(\text{NaO})_2\text{CO} \cdot 2\text{H}_2\text{O}$ , or  $\text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ , "dried sodium carbonate."

$(\text{NaO})_2\text{CO} \cdot 10\text{H}_2\text{O}$ , or  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , crystallized sodium carbonate.

$\text{NaO} \cdot \text{HO} \cdot \text{CO}$ , or  $\text{NaHCO}_3$ , sodium bicarbonate.

$(\text{LiO})_2\text{CO}$ , or  $\text{Li}_2\text{CO}_3$ , lithium carbonate.

$(\text{H}_4\text{NO})_2\text{CO}$ , or  $(\text{H}_4\text{N})_2\text{CO}_3$ , normal ammonium carbonate.

$\text{H}_4\text{NO}.\text{HO}.\text{CO}$ , or  $\text{H}_4\text{NHCO}_3$ , ammonium bicarbonate.

$\text{H}_4\text{NO}.\text{HO}.\text{CO} + \text{H}_4\text{NO}.\text{CO}.\text{H}_2\text{N}$ , ordinary official "carbonate of ammonium" or "hartshorn salt."

$\text{CaO}_2.\text{CO}$ , or  $\text{CaCO}_3$ , calcium carbonate.

$\text{BaO}_2.\text{CO}$ , or  $\text{BaCO}_3$ , barium carbonate.

$\text{FeO}_2.\text{CO}.\text{H}_2\text{O}$ , or  $\text{FeCO}_3.\text{H}_2\text{O}$ , ferrous carbonate.

$(\text{MgO}_2)_3(\text{MgO})_2(\text{HO})_2(\text{CO})_4$ , or  $\text{Mg}_5(\text{OH})_2(\text{CO}_3)_4$ , common official magnesium carbonate.

$(\text{ZnO})_4\text{Zn}(\text{OH})_2(\text{CO})_2$ , or  $\text{Zn}_5(\text{OH})_2(\text{CO}_3)_2$ , common official zinc carbonate.

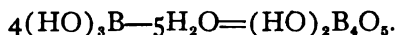
$(\text{PbO}_2)_2\text{Pb}(\text{OH})_2(\text{CO})_2$ , or  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ , common lead carbonate.

$(\text{OBiO})_2\text{CO}.\text{H}_2\text{O}$ , or  $(\text{BiO})_2\text{CO}_3.\text{H}_2\text{O}$ , "subcarbonate of bismuth," or bismuthyl carbonate.

**335. Silicates.** Normal silicic acid is  $(\text{HO})_4\text{Si}$ . The gelatinous silicic acid obtained by decomposing potassium silicate,  $(\text{KO})_4\text{Si}$ , is this normal acid.

Kaolin is  $\text{AlO}_3.\text{HOSi}$ , or  $\text{AlHSiO}_4$ . Solution of sodium silicate ("water glass" or "soluble glass") is supposed to contain  $\text{Na}_2\text{Si}_3\text{O}_7$  and  $\text{Na}_2\text{Si}_4\text{O}_9$ .

**336. Borates.** The only salt of normal boric acid which has a place in any pharmacopœia is glyceryl borate,  $\text{C}_3\text{H}_5\text{BO}_3$ , commonly called "boroglyceride." Borax is  $(\text{NaO})_2\text{B}_4\text{O}_6$ , or  $\text{Na}_2\text{B}_4\text{O}_7$ , with ten molecules of water;  $(\text{HO})_2\text{B}_4\text{O}_6$  is tetraboric acid (also called "pyroboric acid") formed by the separation of water from four molecules of the normal acid when this acid is saturated with a base:



**337. Permanganate** of potassium is  $\text{KOMnO}_3$ , or  $\text{KMnO}_4$ , having a structure analogous to that of potassium perchlorate,  $\text{KOCIO}_3$ , or  $\text{KClO}_4$ .

The *manganate* formed by the reduction of permanganate corresponds to sulphate, the molecular formulas of the potassium salts being  $(\text{KO})_2\text{MnO}_2$ , or  $\text{K}_2\text{MnO}_4$ , and  $(\text{KO})_2\text{SO}_2$ , or  $\text{K}_2\text{SO}_4$ .

**338. Chromates.** Potassium chromate is  $(\text{KO})_2\text{CrO}_2$ , or  $\text{K}_2\text{CrO}_4$ . It is therefore a salt of di-meta-chromic acid and analogous to common potassium sulphate.

Potassium dichromate (or "bichromate of potassium") is

$(\text{KO})_2\text{Cr}_2\text{O}_6$ , or  $\text{K}_2\text{Cr}_2\text{O}_7$ , derived from a meta-acid obtained by splitting off five molecules of water from two molecules of normal chromic acid:



**339. Molybdates.** Ammonium molybdate,  $(\text{H}_4\text{NO})_2\text{MoO}_2$ , or  $(\text{H}_4\text{N})_2\text{MoO}_4$ , is one of the reagents employed in chemical analysis. It will be seen that its composition is analogous to that of the sulphates and chromates.

**340. Tungstates.** Potassium tungstate is  $(\text{KO})_2\text{WO}_2$ , or  $\text{K}_2\text{WO}_4$ , corresponding in structure to the sulphates, chromates and molybdates.

Several meta-acids are known by their sodium salts. They are called "polytungstic" acids. One is  $(\text{HO})_2\text{W}_2\text{O}_6$ , formed by the removal of five molecules of  $\text{H}_2\text{O}$  from two molecules of the normal acid,  $(\text{HO})_6\text{W}$ ; another is  $(\text{HO})_4\text{W}_3\text{O}_7$ , or  $\text{H}_4\text{W}_3\text{O}_{11}$ , formed by removing seven molecules of  $\text{H}_2\text{O}$  from three molecules of normal acid; another, called "meta-tungstic" acid, is formed by the removal of eleven molecules of water from the normal acid, and has the composition  $(\text{HO})_2\text{W}_4\text{O}_{11}$ , or  $\text{H}_2\text{W}_4\text{O}_{15}$ ; and "paratungstic acid" is  $(\text{HO})_{10}\text{W}_{12}\text{O}_{31}$ , or  $\text{H}_{10}\text{W}_{12}\text{O}_{41}$ , formed by removing thirty-one molecules of water from twelve molecules of  $(\text{HO})_6\text{W}$ .

**341. Acetates** of the metals and of ammonium have the structure shown in the following table:

$\text{HO.CO.CH}_3$ , or  $\text{HC}_2\text{H}_3\text{O}_2$ , hydrogen acetate, or acetic acid.  
 $\text{KO.CO.CH}_3$ , or  $\text{KC}_2\text{H}_3\text{O}_2$ , potassium acetate.  
 $\text{NaO.CO.CH}_3$ , or  $\text{NaC}_2\text{H}_3\text{O}_2$ , sodium acetate.  
 $\text{NaO.CO.CH}_3.3\text{H}_2\text{O}$ , crystallized sodium acetate.  
 $\text{H}_4\text{NO.CO.CH}_3$ , ammonium acetate.  
 $\text{MgO}_2(\text{CO})_2(\text{CH}_3)_2$ , or  $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$ , magnesium acetate.  
 $\text{ZnO}_2(\text{CO})_2(\text{CH}_3)_2$ , or  $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ , zinc acetate.  
 $\text{ZnO}_2(\text{CO})_2(\text{CH}_3)_2.3\text{H}_2\text{O}$ , crystallized zinc acetate.  
 $\text{PbO}_2(\text{CO})_2(\text{CH}_3)_2$ , or  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , lead acetate.  
 $\text{PbO}_2(\text{CO})_2(\text{CH}_3)_2.3\text{H}_2\text{O}$ , crystallized lead acetate.  
 $\text{CuO}_2(\text{CO})_2(\text{CH}_3)_2$ , or  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ , copper acetate.  
 $\text{FeO}_3(\text{CO})_3(\text{CH}_3)_3$ , or  $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$ , ferric acetate.  
 $\text{PbO.HO.CO.CH}_3$ , or  $\text{Pb.OH.C}_2\text{H}_3\text{O}_2$ , "subacetate of lead."  
 $\text{CuO.HO.CO.CH}_3$ , or  $\text{Cu.OH.C}_2\text{H}_3\text{O}_2$ , "subacetate of copper."

**342. Valerates**, or valerianates. Valeric acid, or valerianic acid, is  $\text{H}(\text{CH}_2)_4\text{CO.OH}$ , or  $\text{HC}_5\text{H}_9\text{O}_2$ .

$\text{NaC}_5\text{H}_9\text{O}_2$  is sodium valerate.

$\text{H}_4\text{NC}_5\text{H}_9\text{O}_2$  is ammonium valerate.

$\text{Zn}(\text{C}_5\text{H}_9\text{O}_2)_2$  is zinc valerate.

$\text{Fe}(\text{C}_5\text{H}_9\text{O}_2)_3$  is ferric valerate.

**343. Oxalates.** Oxalic acid is  $(\text{HO})_2(\text{CO})_2$ , or  $(\text{CO.OH})_2$ , or  $\text{H}_2\text{C}_2\text{O}_4$ . The student will be able to see that this acid, although composed of a comparatively small number of atoms of each of the same elements that form carbonic acid, differs essentially from the inorganic acids, for it is not a meta-acid derived from normal carbonic acid. That it is an organic acid may be known from the fact that, like acetic acid and valeric acid, it contains the characteristic group  $\text{COOH}$ .

Among the most common oxalates are the following:

$(\text{HO})_2(\text{CO})_2$ , or  $\text{H}_2\text{C}_2\text{O}_4$ , hydrogen oxalate, or oxalic acid.

$(\text{KO})_2(\text{CO})_2$ , or  $\text{K}_2\text{C}_2\text{O}_4$ , normal potassium oxalate.

$\text{KO.HO}(\text{CO})_2$ , or  $\text{KHC}_2\text{O}_4$ , potassium binoxalate.

$(\text{H}_4\text{NO})_2(\text{CO})_2$ , or  $(\text{H}_4\text{N})_2\text{C}_2\text{O}_4$ , ammonium oxalate.

$\text{CaO}_2(\text{CO})_2$ , or  $\text{CaC}_2\text{O}_4$ , calcium oxalate.

$(\text{CeO}_2)_2(\text{CO})_2$ , or  $\text{Ce}_2(\text{C}_2\text{O}_4)_2$ , cerium oxalate.

$(\text{CeO}_2)_2(\text{CO})_2 \cdot 9\text{H}_2\text{O}$ , or  $\text{Ce}_2(\text{C}_2\text{O}_4)_2 \cdot 9\text{H}_2\text{O}$ , cerium oxalate with water.

$\text{FeO}_2(\text{CO})_2$ , or  $\text{FeC}_2\text{O}_4$ , ferrous oxalate.

**344. Tartrates** are the salts of tartaric acid,  $(\text{CHOH.COOH})_2$ , or  $(\text{HO})_2(\text{CO})_2(\text{CHOH})_2$ , or  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ .

$(\text{KO})_2(\text{CO})_2(\text{CHOH})_2$ , or  $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ , potassium tartrate.

$\text{KO.HO}(\text{CO})_2(\text{CHOH})_2$ , or  $\text{KHC}_4\text{H}_4\text{O}_6$ , potassium bitartrate or "cream of tartar."

$\text{KO.NaO}(\text{CO})_2(\text{CHOH})_2$ , or  $\text{KNaC}_4\text{H}_4\text{O}_6$ , with four molecules of water, is "Rochelle salts."

$(\text{NaO})_2(\text{CO})_2(\text{CHOH})_2$ , or  $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ , sodium tartrate.

$(\text{H}_4\text{NO})_2(\text{CO})_2(\text{CHOH})_2$ , or  $(\text{H}_4\text{N})_2\text{C}_4\text{H}_4\text{O}_6$ , ammonium tartrate.

$\text{H}_4\text{NO.HO}(\text{CO})_2(\text{CHOH})_2$ , or  $\text{H}_4\text{NHC}_4\text{H}_4\text{O}_6$ , ammonium bitartrate.

$2[\text{KO.OSbO}(\text{CO})_2(\text{CHOH})_2]\text{H}_2\text{O}$ , or  $2\text{KSbOC}_4\text{H}_4\text{O}_6\text{H}_2\text{O}$ , potassium-antimonyl tartrate, or tartar emetic.

**345. Citrates** are formed by the acid  $(\text{CH}_2)_2\text{COH}(\text{COOH})_3$ , or  $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ .

$(\text{HO})_3(\text{CO})_3\text{COH}(\text{CH}_2)_2\text{H}_2\text{O}$ , or  $\text{H}_3\text{C}_6\text{H}_5\text{O}_7\cdot\text{H}_2\text{O}$ , hydrogen citrate or citric acid.

$(\text{KO})_3(\text{CO})_3\text{COH}(\text{CH}_2)_2\text{H}_2\text{O}$ , or  $\text{K}_3\text{C}_6\text{H}_5\text{O}_7\cdot\text{H}_2\text{O}$ , potassium citrate.

$(\text{NaO})_3(\text{CO})_3\text{COH}(\text{CH}_2)_2$ , or  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ , sodium citrate.

$(\text{NaO})_2\text{HO}(\text{CO})_3\text{COH}(\text{CH}_2)_2$ , or  $\text{Na}_2\text{HC}_6\text{H}_5\text{O}_7$ , di-sodium hydrogen citrate.

$\text{NaO}(\text{HO})_2(\text{CO})_3\text{COH}(\text{CH}_2)_2$ , or  $\text{NaH}_2\text{C}_6\text{H}_5\text{O}_7$ , sodium di-hydrogen citrate.

$(\text{H}_4\text{NO})_3(\text{CO})_3\text{COH}(\text{CH}_2)_2$ , or  $(\text{H}_4\text{N})_3\text{C}_6\text{H}_5\text{O}_7$ , ammonium citrate.

$(\text{H}_4\text{NO})_2\text{HO}(\text{CO})_3\text{COH}(\text{CH}_2)_2$ , or  $(\text{H}_4\text{N})_2\text{HC}_6\text{H}_5\text{O}_7$ , di-ammonium hydrogen citrate.

$\text{H}_4\text{NO}(\text{HO})_2(\text{CO})_3\text{COH}(\text{CH}_2)_2$ , or  $\text{H}_4\text{NH}_2\text{C}_6\text{H}_5\text{O}_7$ , ammonium di-hydrogen citrate.

$(\text{LiO})_3(\text{CO})_3\text{COH}(\text{CH}_2)_2$ , or  $\text{Li}_3\text{C}_6\text{H}_5\text{O}_7$ , lithium citrate.

$(\text{LiO})_3(\text{CO})_3\text{COH}(\text{CH}_2)_2\cdot 4\text{H}_2\text{O}$ , lithium citrate with water.

$(\text{MgO}_2)_3(\text{CO})_3(\text{COH})_2(\text{CH}_2)_4$ , magnesium citrate.

$\text{MgO}_2\text{HO}(\text{CO})_3\text{COH}(\text{CH}_2)_2$ , acid magnesium citrate.

$\text{FeO}_3(\text{CO})_3\text{COH}(\text{CH}_2)_2$ , ferric citrate.

$\text{BiO}_3(\text{CO})_3\text{COH}(\text{CH}_2)_2$ , bismuth citrate.

**346. Lactates** are the salts of  $\text{CH}_3\text{CHOHCOOH}$ , or  $\text{HO}\cdot\text{CO}\cdot\text{CHOH}\cdot\text{CH}_2\cdot\text{H}$ , or  $\text{HC}_3\text{H}_5\text{O}_3$ .

$\text{HO}\cdot\text{CO}\cdot\text{CHOH}\cdot\text{CH}_3$ , hydrogen lactate or lactic acid.

$\text{NaO}\cdot\text{CO}\cdot\text{CHOH}\cdot\text{CH}_3$ , or  $\text{NaC}_3\text{H}_5\text{O}_3$ , sodium lactate.

$\text{CaO}_2(\text{CO})_2(\text{CHOH})_2(\text{CH}_3)_2$ , or  $\text{Ca}(\text{C}_3\text{H}_5\text{O}_3)_2$ , calcium lactate.

$\text{ZnO}_2(\text{CO})_2(\text{CHOH})_2(\text{CH}_3)_2\cdot 3\text{H}_2\text{O}$ , or  $\text{Zn}(\text{C}_3\text{H}_5\text{O}_3)_2\cdot 3\text{H}_2\text{O}$ , zinc lactate.

$\text{FeO}_2(\text{CO})_2(\text{CHOH})_2(\text{CH}_3)_2\cdot 3\text{H}_2\text{O}$ , or  $\text{Fe}(\text{C}_3\text{H}_5\text{O}_3)_2\cdot 3\text{H}_2\text{O}$ , ferrous lactate.

**347. Salicylates** have the following structure:

$\text{HO}\cdot\text{C}_7\text{H}_5\text{O}_2$ , or  $\text{HC}_7\text{H}_5\text{O}_3$ , salicylic acid.

$2\text{NaC}_7\text{H}_5\text{O}_3\cdot\text{H}_2\text{O}$ , sodium salicylate.

$2\text{LiC}_7\text{H}_5\text{O}_3\cdot\text{H}_2\text{O}$ , lithium salicylate.

$\text{Zn}(\text{C}_7\text{H}_5\text{O}_3)_2\cdot 3\text{H}_2\text{O}$ , zinc salicylate.

$\text{Hg}(\text{C}_7\text{H}_5\text{O}_3)_2$ , mercuric salicylate.

$\text{Bi}(\text{C}_7\text{H}_5\text{O}_3)_3$ , bismuth salicylate.

**348. Phenolsulphonates** (commonly called "sulpho-carbolates"). Phenolsulphonic acid is  $C_6H_4.OH.HSO_3$ , or  $HC_6H_5SO_3$ .

$NaC_6H_5SO_3.2H_2O$ , sodium phenolsulphonate.

$Ca(C_6H_5SO_3)_2$ , calcium phenolsulphonate.

$Ba(C_6H_5SO_3)_2$ , barium phenolsulphonate.

$Zn(C_6H_5SO_3)_2.8H_2O$ , zinc phenolsulphonate.

**349. Benzoates** are the salts of  $HC_7H_5O_2$ .

$HC_7H_5O_2$ , hydrogen benzoate, or benzoic acid.

$NaC_7H_5O_2$ , sodium benzoate.

$LiC_7H_5O_2$ , lithium benzoate.

$H_4NC_7H_5O_2$ , ammonium benzoate.

$Ca(C_7H_5O_2)_2$ , calcium benzoate.

$Fe(C_7H_5O_2)_3$ , ferric benzoate.

**350. Oleates** are the salts formed by the fat-acid  $HC_{18}H_{33}O_2$ .

$KC_{18}H_{33}O_2$  is potassium oleate.

$NaC_{18}H_{33}O_2$ , sodium oleate.

$Zn(C_{18}H_{33}O_2)_2$ , zinc oleate.

$Pb(C_{18}H_{33}O_2)_2$ , lead oleate.

$Cu(C_{18}H_{33}O_2)_2$ , copper oleate.

$Hg(C_{18}H_{33}O_2)_2$ , mercuric oleate.

$Fe(C_{18}H_{33}O_2)_3$ , ferric oleate.

$Al(C_{18}H_{33}O_2)_3$ , aluminum oleate.

$Bi(C_{18}H_{33}O_2)_3$ , bismuth oleate.

## CHAPTER XVII.

### CHEMICAL REACTIONS.

**351. The relative stability of molecules.** The molecules of matter remain unaltered under constant or unchanged conditions.

All matter is subject to the influence of the various forms of physical and chemical energy.

The stability of molecules depends upon an equilibrium of the forces affecting them, and the universal tendency of matter is the attainment of that equilibrium.

Atoms of matter always tend toward the formation of such molecules as may offer the greatest resistance to change under whatever conditions may prevail at the time. When these conditions are changed so that the former equilibrium is destroyed, the molecules are disrupted, the atoms are rearranged into new molecules in accord with a new equilibrium and, of all the new molecules possible, those are formed which may best resist further change under the new conditions.

**352.** Chemical changes are called **chemical reactions**. They are rearrangements of the atomic linking in the molecules of matter.

Any change which takes place within a molecule is a chemical reaction.

**353.** The molecules of different kinds of matter differ according to the number, kind, and relative position of their atoms.

The removal of one or more atoms from any molecule is a chemical reaction and results in a new and different molecule or a new kind of matter.

The addition or insertion of one or more atoms into any molecule is also a chemical reaction whereby a new kind of matter is formed.

The replacement of one or more atoms of any molecule by any other atom or atoms is likewise a chemical reaction.

Any interatomic rearrangement within a molecule by which the relative position of any one or more of its atoms may be altered, without any change in the kind or number of said atoms is also a chemical reaction.

**354.** One single molecule may be altered as to its internal or atomic structure and thus become transformed into a new and different molecule.

Or one molecule may be split up into two or more new molecules.

Or two or more molecules of the same kind may be condensed into one new molecule; but not by mere addition or simple union for the coalescence involves a rearrangement of the atomic linking.

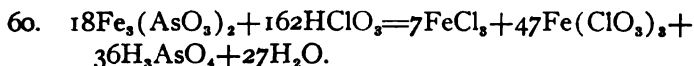
Or two or more molecules of different kinds may be caused to unite or coalesce into one or more new molecules of one kind, also by a rearrangement of the atomic linking.

Or two or more different kinds of molecules may react upon each other and together produce two or more new kinds of molecules.

**355.** The following equations representing examples of chemical reactions may be studied and the apparent differences between them noted by the student:

1.  $\text{Fe} + 2\text{I} = \text{FeI}_2.$
2.  $\text{Fe} + 3\text{Cl} = \text{FeCl}_3.$
3.  $2\text{H} + \text{O} = \text{H}_2\text{O}.$
4.  $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}.$
5.  $\text{Hg} + \text{O} = \text{HgO}.$
6.  $2\text{Hg} + \text{O}_2 = 2\text{HgO}.$
7.  $\text{HgO} = \text{Hg} + \text{O}.$
8.  $2\text{HgO} = 2\text{Hg} + \text{O}_2.$
9.  $\text{K} + \text{Cl} = \text{KCl}.$
10.  $\text{FeCl}_2 + \text{Cl} = \text{FeCl}_3.$
11.  $2\text{FeCl}_3 + \text{Fe} = 3\text{FeCl}_2.$
12.  $\text{CO} + \text{O} = \text{CO}_2.$
13.  $2\text{CO} + \text{O}_2 = 2\text{CO}_2.$
14.  $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}.$
15.  $3\text{H}_2\text{O}_2 = 3\text{H}_2\text{O} + \text{O}_3.$
16.  $\text{CaCO}_3 = \text{CaO} + \text{CO}_2.$
17.  $\text{CaO} + \text{CO}_2 = \text{CaCO}_3.$
18.  $\text{Ca}(\text{OH})_2 = \text{CaO} + \text{H}_2\text{O}.$
19.  $\text{CaO} + \text{H}_2\text{O} = \text{Ca}(\text{OH})_2.$
20.  $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_3.$
21.  $\text{SO}_3 + 2\text{H}_2\text{O} = \text{H}_4\text{SO}_5.$

22.  $\text{SO}_3 + 3\text{H}_2\text{O} = \text{H}_6\text{SO}_6.$
23.  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} = \text{H}_4\text{SO}_6.$
24.  $\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} = \text{H}_6\text{SO}_6.$
25.  $6\text{P} + 5\text{I} + 25\text{Br} = \text{PI}_5 + 5\text{PbBr}_5.$
26.  $\text{Na}_2\text{SO}_3 + \text{S} = \text{Na}_2\text{S}_2\text{O}_3.$
27.  $\text{H}_3\text{N} + \text{HCl} = \text{H}_4\text{NCl}.$
28.  $2\text{H}_3\text{N} + \text{H}_2\text{SO}_4 = (\text{H}_4\text{N})_2\text{SO}_4.$
29.  $\text{MnO}_2 + 2\text{SO}_2 = \text{MnS}_2\text{O}_6.$
30.  $\text{C}_2\text{H}_4\text{O} + \text{O} = \text{HC}_2\text{H}_5\text{O}_2.$
31.  $\text{C}_2\text{H}_4 + \text{Br}_2 = \text{C}_2\text{H}_4\text{Br}_2.$
32.  $3\text{CH}_3\text{O} = \text{C}_3\text{H}_9\text{O}_3.$
33.  $\text{H}_2\text{O} + \text{K} = \text{KOH} + \text{H}.$
34.  $2\text{H}_2\text{O} + \text{K}_2 = 2\text{KOH} + \text{H}_2.$
35.  $\text{H}_2\text{O} + \text{Cl}_2 = 2\text{HCl} + \text{O}.$
36.  $2\text{H}_2\text{O} + 2\text{Cl}_2 = 4\text{HCl} + \text{O}_2.$
37.  $\text{Zn} + 2\text{HCl} = \text{ZnCl}_2 + \text{H}_2.$
38.  $\text{ZnO} + 2\text{HCl} = \text{ZnCl}_2 + \text{H}_2\text{O}.$
39.  $\text{Fe}_2\text{O}_3 + 3\text{H}_2 = 2\text{Fe} + 3\text{H}_2\text{O}.$
40.  $\text{Sb}_2\text{S}_3 + 9\text{O} = \text{Sb}_2\text{O}_3 + 3\text{SO}_2.$
41.  $\text{KClO}_4 = \text{KCl} + 2\text{O}_2.$
42.  $4\text{KClO}_3 = 3\text{KClO}_4 + \text{KCl}.$
43.  $\text{Pb}_3\text{H}_2(\text{CO}_4)_2 = 3\text{PbO} + \text{H}_2\text{O} + 2\text{CO}_2.$
44.  $\text{Sb}_2\text{S}_3 + 3\text{Na}_2\text{S} + \text{S}_2 = 2\text{Na}_3\text{SbS}_4.$
45.  $\text{Na}_2\text{S}_2\text{O}_8 + 2\text{HCl} = 2\text{NaCl} + \text{SO}_2 + \text{S} + \text{H}_2\text{O}.$
46.  $\text{Na}_2\text{S} + \text{Na}_2\text{SO}_3 + \text{I}_2 = \text{Na}_2\text{S}_2\text{O}_8 + 2\text{NaI}.$
47.  $6\text{KHSO}_5 + 2\text{S} = 2\text{K}_2\text{S}_2\text{O}_8 + \text{K}_2\text{S}_2\text{O}_8 + 3\text{H}_2\text{O}.$
48.  $\text{HNO}_3 + 3\text{HCl} = \text{NOCl} + 2\text{H}_2\text{O} + \text{Cl}_2.$
49.  $\text{H}_2\text{SO}_4 + 2\text{HBr} = \text{SO}_2 + \text{Br}_2 + 2\text{H}_2\text{O}.$
50.  $\text{FeCl}_3 + \text{KI} = \text{I} + \text{FeCl}_2 + \text{KCl}.$
51.  $2\text{C}_2\text{H}_5\text{OH} + 2\text{FeCl}_3 = \text{C}_2\text{H}_4\text{O} + \text{C}_2\text{H}_5\text{Cl} + 2\text{FeCl}_2 + \text{HCl} + \text{H}_2\text{O}.$
52.  $\text{C}_2\text{H}_5\text{OH} + \text{Cl}_2 = \text{C}_2\text{H}_4\text{O} + 2\text{HCl}.$
53.  $\text{C}_2\text{H}_5\text{OH} + \text{HCl} = \text{C}_2\text{H}_5\text{Cl} + \text{H}_2\text{O}.$
54.  $2\text{K}_2\text{H}_3\text{O}_2 + 8\text{O} = \text{K}_2\text{CO}_3 + 3\text{H}_2\text{O} + 3\text{CO}_2.$
55.  $5\text{Fe}(\text{PH}_2\text{O}_2)_3 + 12\text{KMnO}_4 + 18\text{H}_2\text{SO}_4 = 5\text{FePO}_4 + 10\text{H}_3\text{PO}_4 + 6\text{K}_2\text{SO}_4 + 12\text{MnSO}_4 + 18\text{H}_2\text{O}.$
56.  $3\text{Sb}_2\text{S}_3 + 28\text{HNO}_3 = 3\text{Sb}_2\text{O}_3 + 9\text{H}_2\text{SO}_4 + 28\text{NO} + 5\text{H}_2\text{O}.$
57.  $6\text{Sb} + 10\text{HNO}_3 = 3\text{Sb}_2\text{O}_3 + 10\text{NO} + 5\text{H}_2\text{O}.$
58.  $\text{Pb}(\text{NO}_3)_2 + 6\text{KOH} + 6\text{Al} = \text{Pb} + 2\text{H}_3\text{N} + 3\text{K}_2\text{Al}_2\text{O}_4.$
59.  $18\text{Fe}(\text{OH})_2 + 54\text{HClO}_3 = \text{FeCl}_3 + 17\text{Fe}(\text{ClO}_3)_3 + 45\text{H}_2\text{O}.$



**356.** The transformation of one single molecule into another single molecule of a different kind, and that of any number of molecules of but one kind into any number of molecules of other kinds; are of less frequent occurrence than the mutual chemical reactions which take place between two or more different kinds of molecules.

**357.** In general the highest attainable degree of saturation of chemical energy is conducive to the greatest attainable stability or resistance to change. In other words, under conditions which are in all other respects the same, those molecules in which the most powerful positive radicals are united to the most powerful negative radicals are the most stable molecules.

**358.** The **factors** of chemical reactions are the molecules which take part in them.\*

In a great majority of the common reactions of inorganic chemistry there are but two kinds of reacting molecules or factors. In many other reactions there are three factors.

Reactions in which only one kind of molecules undergo chemical change independently of other molecules are comparatively uncommon.

Reactions between more than three factors are also unusual.

**359.** The new molecules formed by chemical reactions are called the **products**.

The number of products formed by one single reaction is in most cases two or three. But in many reactions there is but one product, and in others more than three.

When two or more products result from the reaction, one of them is usually the *principal product* sought, and any additional products formed in such cases are called *bye-products*.

**360.** The great majority of the reactions performed in the laboratory may be grouped under six principal heads:

1. **Intramolecular reactions**, or *metastases*, which are rearrangements of the atoms within a single kind of molecules.

Such reactions are rare, but occur in organic chemistry.

\* The factors of chemical reactions are also called "reagents"; but this term is rarely used except in analytical chemistry where it is applied to substances employed for the identification or detection of individual elements, radicals (ions) and compounds by means of the characteristic reactions which they produce with the reagents.

2. **Dissociation** means the splitting or division of one or more molecules of one kind into molecules of two or more other kinds.\*

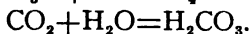
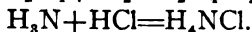
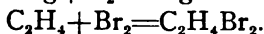
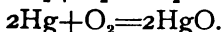
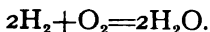
Dissociation is simple decomposition.

3. **Condensation** reactions are chemical changes by which two or more molecules of one kind are condensed into new molecules of the same percentage composition but having a molecular weight which is a simple multiple of that of the original molecules. But condensation unaccompanied by a change of the atomic linking is not a true chemical change.

Common aldehyde,  $C_2H_4O$ , is changed by condensation into paraldehyde, which is  $C_6H_{12}O_6$ .†

4. **Synthesis**, or a synthetic reaction, is the direct union of two or more elements into one kind of compound molecules, or the rearrangement of the atoms of two or more kinds of molecules into new molecules of but one kind.

The following are synthetic reactions:



Hence synthetic reactions result in but one product.

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\* Reactions of dissociation have also been called "analytical reactions" or "analyses"; but these terms are now employed exclusively in analytical chemistry to designate the characteristic qualitative and quantitative test-reactions and other analytical processes by which the identity, composition and purity of substances may be determined.

† Two or more compounds may have exactly the same percentage composition, containing the same elements in precisely the same proportions, and yet these compounds may exhibit widely different properties.

Morphine and piperin are totally different substances; yet both of them have the composition represented by the molecular formula  $C_{17}H_{19}NO_5$ .

Formaldehyde and acetic acid are both represented by the empiric formula  $CH_2O$ , and paraformaldehyde is  $(CH_2O)_n$ .

Hemiterpenes have the composition  $C_5H_8$ , terpenes  $C_{10}H_{16}$ , sesquiterpenes  $C_{15}H_{24}$ , and diterpenes  $C_{20}H_{32}$ .

Different substances having the same percentage composition are called isomers, or are isomeric compounds.

Isomeric compounds which contain not only the same kinds of atoms in the same relative proportions but exactly the same number of atoms of each kind, so that they also have the same molecular weights, are called metamers or metameric compounds.

Compounds containing the same elements in the same relative proportions but of which the molecular weight of one is double or treble that of the other are called polymers or pleomers.

5. **Metatheses**, or metathetic. reactions are chemical reactions between molecules of two or more kinds resulting in the formation of two or more products.

When metathesis occurs between two factors both of which are compound molecules and a mutual or double interchange of radicals (or ions) is thus effected, the reaction is called *double decomposition*.

When metathesis results in the substitution of one element or compound radical for another in the molecule of the principal product the reaction is called *substitution*, and the principal product thus formed is called a "substitution product."

6. **Reactions of oxidation and reduction**, described in paragraph 370.

**361.** Metastases and condensation reactions occur in organic chemistry.

Substitution reactions occur very frequently both in inorganic and in organic chemistry, although the general term "metathesis" is commonly employed to designate such reactions in inorganic chemistry, and the terms "substitution" and "substitution products" are used in organic chemistry.

Dissociation, synthesis, and metathesis are common reactions, but the most common are metatheses.

**362.** **Dissociation** effected by the aid of heat is often a most convenient means of producing inorganic chemical products.

Compound molecules may be split up by heat into elemental molecules (as when mercuric oxide is decomposed into mercury and oxygen), or into new compound molecules; or the products may include both elemental and compound molecules.

All metallic carbonates, except the alkali carbonates, are decomposed by strong heat. When calcium carbonate ( $\text{CaCO}_3$ ) is "calcined," or strongly heated, as in a "lime kiln," it breaks up into calcium oxide ( $\text{CaO}$ ) and carbon dioxide ( $\text{CO}_2$ ); and when the basic magnesium carbonate of the pharmacopœia is "calcined" it splits up into three kinds of compound molecules which are magnesium oxide ( $\text{MgO}$ ), carbon dioxide ( $\text{CO}_2$ ), and water ( $\text{H}_2\text{O}$ ).

In the production of charcoal from wood we see an illustration of dissociation resulting in the formation of several products, one of which is the element carbon; but it must be remembered that wood is a mixture.

**363.** Dissociation is frequently attended by changes of polarity-value of one or more of the component elements of the molecule decomposed. In other words, dissociation is often accompanied by "oxidation" and "reduction."

Potassium chlorate contains the element chlorine with a polarity-value of  $+5$ ; but when it is strongly heated it undergoes dissociation and one of the products is potassium chloride, in which the polarity-value of the chlorine is  $-1$ .

Lead nitrate contains nitrogen, the polarity-value of which is  $+5$ ; but one of the products of its dissociation is  $\text{NO}_2$ , containing all the nitrogen of the decomposed nitrate with a polarity-value of  $+4$ .

Ammonium nitrate contains two nitrogen atoms, one of which has the polarity-value  $+5$  and the other the polarity-value  $-3$ ; both of these nitrogen atoms enter into the decomposition product  $\text{N}_2\text{O}$  when the salt is heated to dissociation, and the polarity-value of the N in  $\text{N}_2\text{O}$  is  $+1$ .

When any compound molecule is decomposed into its elements, or when one or more of the products of dissociation is an element, there is oxidation and reduction.

**364. Synthetic reactions**, or syntheses, appear to be simple additions such as might be represented by the equation  $1+2=3$ .

Thus hydrogen and chlorine unite to form hydrogen chloride or hydrochloric acid; and iron and iodine unite in the presence of water to form ferrous iodide.

Ammonia seems to combine directly with hydrochloric acid to form ammonium chloride, and calcium oxide with carbon dioxide to form calcium carbonate.

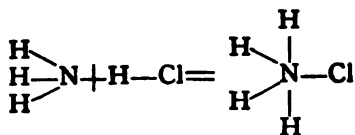
In each of these four synthetic reactions two kinds of molecules unite to form but one product.

But syntheses are in most cases, if not always, less simple than they seem to be. Even when two elements appear to unite directly the elemental molecules must be decomposed into their constituent atoms (unless the molecules are monatomic) before these dissociated atoms can enter into the formation of the compound molecules.

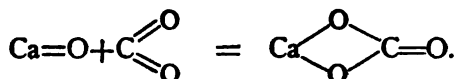
Thus the reaction between hydrogen and chlorine by which hydrochloric acid is formed can not be fully represented by  $\text{H}+\text{Cl}=\text{HCl}$ , but must be  $\text{H}_2+\text{Cl}_2=2\text{HCl}$ .

When ammonia and hydrochloric acid form ammonium chloride

the change in the atomic linking can be seen only when the reaction is represented by the structural formulas:



The following reaction also readily discloses a change of atomic connections:



**365.** Whenever the factors of a synthetic reaction are elements, or when one of them is an element, oxidation and reduction take place in the reaction.

Thus, when hydrogen and chlorine unite to form hydrochloric acid the hydrogen acquires a positive polarity-value and the chlorine acquires a negative polarity-value.

Oxidation and reduction do not attend synthetic reactions when the factors are compound molecules. But such reactions may be accompanied by changes of valence. Thus when  $\text{H}_3\text{N}$  unites with  $\text{HCl}$  the trivalent N of the  $\text{H}_3\text{N}$  becomes quinquivalent N in the product  $\text{H}_4\text{NCl}$ , while the polarity-value of the N in both  $\text{H}_3\text{N}$  and  $\text{H}_4\text{NCl}$  is the same, namely  $-3$ .

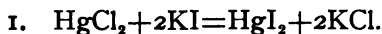
**366. Metatheses** are very common reactions, and, when not accompanied by oxidation and reduction, they are simple and readily understood.

The products of metathetic reactions have in most cases the same general molecular structure as the reacting substances, and this is especially true of double decompositions.

**367. Double decomposition.** In reactions of this kind the two factors simply change partners. There is a double or mutual interchange of radicals (or ions).

Regarding the molecules of both the factors and the products as being, each of them, composed of two radicals (or ions), one positive and the other negative, these radicals are readily seen to remain precisely the same after the reaction as before, but simply transposed. We may, therefore, in a way, liken metathesis to an interchange of partners by two couples, or to an exchange of

horses by two riders, as shown in the following representative examples:



In this "chemical equation" the Hg and the K are the positive radicals; the Cl and the I are the negative radicals.

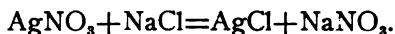
We will call the positive radicals riders and the negative radicals horses.

Hg, riding the horse Cl, meets K, riding the horse I; the riders exchange horses.

2. Silver nitrate contains the positive radical silver, Ag, and the negative radical  $\text{NO}_3$ , called the "nitrate radical."

Sodium chloride is composed of the positive radical sodium, Na, and the negative radical chlorine, Cl.

When silver nitrate and sodium chloride are brought into contact with each other, each in a state of solution in water, they mutually react upon each other and the products are sodium nitrate and silver chloride:

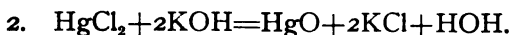


The student will see that the radicals of the first member of this chemical equation are Ag,  $\text{NO}_3$ , Na and Cl, and that the radicals of the second member of the equation are precisely the same. Thus we start with a nitrate and a chloride, and after the reaction we still have a nitrate and a chloride. Our factors were a silver salt and a sodium salt; and our products, too, are a silver salt and a sodium salt. But our riders have exchanged horses; instead of silver nitrate and sodium chloride we have silver chloride and sodium nitrate.

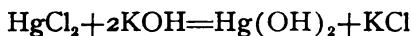
**368.** But there are numerous reactions in which the metathesis is not so simple or apparent, as when the factors or the products are more than two.



Here the K of KOH and the Na of NaOH both unite with the  $\text{C}_2\text{O}_4$  of the  $\text{H}_2\text{C}_2\text{O}_4$ , and the OH of both KOH and NaOH together with the H<sub>2</sub> of the  $\text{H}_2\text{C}_2\text{O}_4$  form 2HOH.

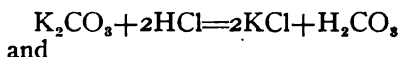


In this reaction the Hg combines with one atom of O from the KOH, because Hg does not combine with OH. But if the student assume that the reaction is



and that the  $\text{Hg}(\text{OH})_2$  instantly splits up into HgO and  $\text{H}_2\text{O}$ , the whole process may be regarded as a simple metathesis followed by the dissociation of one of the products.

3.  $\text{K}_2\text{CO}_3 + 2\text{HCl} = 2\text{KCl} + \text{HOH} + \text{CO}_2$  may also be regarded as the summary of two reactions, namely



and



Further examples of metathetic and other reactions will be given in the chapter on how to write chemical equations.

**389. Substitution** occurs in the production of inorganic chemicals chiefly in the chemical solution of metals in acids; but also in other reactions.

1.  $\text{Zn} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2.$
2.  $\text{K}_2 + 2\text{HOH} = 2\text{KOH} + \text{H}_2.$
3.  $\text{Zn} + 2\text{KOH} = \text{Zn}(\text{OK})_2 + \text{H}_2.$
4.  $\text{FeCl}_2 + \text{Zn} = \text{ZnCl}_2 + \text{Fe}.$
5.  $2\text{Al} + 6\text{HCl} = 2\text{AlCl}_3 + 3\text{H}_2.$

## CHAPTER XVIII.

### OXIDATION AND REDUCTION.

**370.** More complex than any other reactions are those by which one or more atoms acquire increased polarity-value while one or more other atoms suffer a corresponding decrease of polarity-value. Such reactions are called **reactions of oxidation and reduction.**

*Oxidation* is an increase in the algebraic sum of the units of polarity-value of any element.

*Reduction* is a diminution of the algebraic sum of the units of polarity-value of any element.

Oxidation and reduction are each the opposite of the other.

**371.** All reactions in which elemental molecules constitute one or more of either the factors or the products, or both, are nearly always reactions of oxidation and reduction since free elements have no actual valence or polarity-value while combined atoms have occupied bonds or combining units which may be either positive or negative, or a part of them positive and the remainder negative.

But an atom in combination may have a polarity-value of 0, and when such an atom is liberated from a compound that atom is neither oxidized nor reduced.

**372.** The factors of reactions of oxidation and reduction may be one, or two, or three, or even more; and the products, too, may be one or two or three or more.

When both factors and products exceed two each, and when they are all compound molecules, the reactions of oxidation and reduction may appear very complicated.

**373.** Reactions of oxidation and reduction may be dissociations, syntheses, or metatheses; but metatheses are not readily identified as such when complicated by changes of polarity-value of component elements of the factors and products.

**374.** Oxidation may be the result of an increase in the number of units of atomic combining value of positive polarity; or a decrease in the number of units of atomic combining value of

negative polarity; or a change of the polarity-value of any element from zero to a plus-quantity; or a change of its polarity-value from a minus-quantity to zero; or the complete reversal of the polarity of an element from negative to positive.

The following examples illustrate oxidation:

1. The iron atom in  $\text{FeCl}_2$  has a polarity-value of  $+2$ . When the  $\text{FeCl}_2$  is changed to  $\text{FeCl}_3$  the iron atom acquires a polarity-value of  $+3$ . It has, therefore, been oxidized. It also gained one additional bond.

2. The carbon atom in  $\text{H}_4\text{C}$  has a polarity-value of  $-4$ . When the  $\text{H}_4\text{C}$  is changed to  $\text{H}_3\text{CCl}$  the polarity-value of the carbon becomes  $-2$  because that atom is now united by three combining units of negative polarity to the three hydrogen atoms and by one combining unit of positive polarity to the chlorine atom; the polarity-value of any atom is the algebraic sum of its positive and negative combining units, and the algebraic sum of  $-3$  and  $+1$  is  $-2$ .

The change in the polarity-value of the carbon atom from  $-4$  to  $-2$  is an *increase*, and is oxidation. But the carbon has the same number of bonds as before.

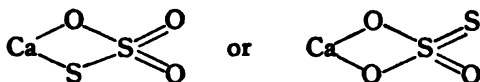
3. As the polarity-value of any free atom is 0, that atom is oxidized whenever it assumes positive polarity, which it does when it enters into combination with any atom of negative polarity. An atom of hydrogen is oxidized whenever it combines with any other element because hydrogen never exercises negative polarity. Hence when hydrogen and chlorine form hydrochloric acid the hydrogen is oxidized.

4. In the molecule of water, or in any other compound molecule containing oxygen, the oxygen has a polarity-value of  $-2$ , except where two or more oxygen atoms are united to each other in which event one or more of those atoms necessarily have a polarity-value of 0. Whenever that oxygen is liberated it assumes a polarity-value of 0, whether it be regarded as free atoms or as consisting of diatomic molecules (ordinary oxygen) or of triatomic molecules (ozone). Hence, whenever oxygen (or any other element of negative polarity) is liberated from any one of its compounds, it is oxidized. Thus when  $\text{HgO}$  breaks up into  $\text{Hg}$  and  $\text{O}$ , the oxygen is oxidized, but the  $\text{Hg}$  and the  $\text{O}$  lose 2 bonds each.

5. When ammonia is converted into nitric acid the nitrogen

of the  $H_3N$  is oxidized, because its polarity-value in  $HONO_2$  is  $+5$ , while in the  $H_3N$  it was  $-3$ . The polarity of the N has been completely reversed, and as it changed from negative to positive it was oxidized; but acquired 2 new bonds.

6. When sulphur is boiled with calcium hydroxide in water it forms molecules of  $CaS_2O_3$  in which one of the two sulphur atoms exercises a polarity-value of  $+6$ , while the other has a polarity-value of  $-2$ . As the uncombined sulphur had a polarity-value of 0, one-half of it is oxidized and the other half is reduced in forming  $CaS_2O_3$ , for the structure of that molecule is either



but both of the atoms of S gained bonds.

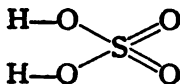
But when two or more sulphur atoms are united directly in a polyatomic molecule it may be the case that one or more of those atoms in combination have a polarity-value of 0.

**375. Reduction** means an increase in the number of units of atomic combining value of negative polarity; or a decrease in the number of units of combining value of positive polarity; or a change of the polarity-value of an atom from 0 to a minus quantity; or a change of its polarity-value from a plus quantity to 0; or the complete reversal of the polarity of the atom from positive to negative.

The following examples will suffice:

1. The mercury atom in  $HgCl_2$  has a polarity-value of  $+2$ . When the  $HgCl_2$  is converted into  $HgCl$  by the removal of one of the chlorine atoms the mercury atom attains a polarity-value of  $+1$ . Its value was, therefore, reduced. It also lost 1 bond.

2. When sulphuric acid is strongly heated with charcoal the  $H_2SO_4$  is decomposed and the gas  $SO_2$  evolved. The sulphur atom in



has a polarity valence of  $+6$ , but the sulphur in  $O=S=O$  has a

polarity-value of only  $+4$ . A reduction, therefore, occurred in this reaction. The S also lost 2 bonds.

3. The polarity-value of a free atom being 0, it is reduced whenever that atom assumes negative polarity which it does when it enters into combination with a positive element. Whenever an atom of oxygen enters into combination with any other element the oxygen atom suffers reduction because oxygen in combination is always of negative polarity. But while the oxygen atom lost polarity-value it gained two bonds.

4. When zinc attacks hydrochloric acid, enters into combination with the chlorine, and sets the hydrogen free, the zinc is oxidized and the hydrogen reduced, for the zinc changes its polarity-value from 0 to  $+2$ , while the hydrogen changes its polarity-value from  $+1$  to 0.

Whenever hydrogen, or any other element of positive polarity, is liberated from any one of its compounds it is thereby reduced.

5. When  $\text{KOCIO}_2$  is strongly heated it suffers dissociation. The products are  $\text{KCl}$  and  $3\text{O}$ . The chlorine in the  $\text{KOCIO}_2$  has a polarity-value of  $+5$ , but in  $\text{KCl}$  its value is  $-1$ ; the chlorine was, therefore, reduced. The oxygen in the  $\text{KOCIO}_2$  had a polarity-value of  $-2$ ; when liberated that value was increased to 0.

6. When iodine is dissolved in a solution of  $\text{KOH}$  the products formed by the iodine are  $\text{KI}$  and  $\text{KIO}_3$ . The iodine used had a polarity-value of 0; in  $\text{KI}$  its polarity-value is  $-1$ ; and in  $\text{KIO}_3$  it is  $+5$ . Therefore so much of the iodine as entered into the formation of  $\text{KI}$  was reduced, but the iodine which formed the  $\text{KIO}_3$  was oxidized; but all of the iodine atoms acquired bonds which they did not have as *free* atoms.

**376.** Oxidation and reduction always occur together.

There can be no oxidation of any atom or atoms without corresponding reduction of another atom or other atoms.

In every transfer of units of polarity-value (called "oxidation and reduction") *the number of units gained by the atom or atoms oxidized is the number of units lost by the atom or atoms reduced.*

**377.** In reactions of oxidation and reduction the elements reduced are called the **oxidizing agents**.

There may be one or more oxidizing agents in the same reaction.

The most effective oxidizing agents are elements having a high

polarity-value and, therefore, capable of considerable reduction. Thus the nitrogen of nitrates, having a polarity-value of +5, the chlorine of chlorates with a polarity-value of +5, or of perchlorates with a polarity-value of +7, the manganese of permanganates having a polarity-value of +7, the chromium of chromates which has a polarity-value of +6 — these are all of them powerful oxidizing agents.

Free elements of great intensity of chemical energy, and which assume negative polarity when entering into combination, are also effective oxidizing agents. Oxygen and chlorine are such elements.

**378.** In reactions of oxidation and reduction the elements oxidized, or which gain polarity-value, are called the **reducing agents**.

The most effective reducing agents are elements having a low polarity-value and capable of considerable oxidation. Thus the sulphur of  $\text{SO}_2$  is a reducing agent because it has a polarity-value of +4 capable of being raised to +6.

**379.** Elements having a variable valence may be reducing agents when they have a lower polarity-value, and they may be oxidizing agents when they have a higher polarity-value.

Thus in any reaction whereby a ferrous compound is changed to a ferric compound the iron acts as a reducing agent and is oxidized because the iron in ferrous compounds has a polarity-value of only +2, while the iron in ferric compounds has a polarity-value of +3. But in any reaction whereby a ferric compound is changed to a ferrous compound, the iron acts as an oxidizing agent and is reduced for it gives up one of its positive bonds.

**380.** When powerful oxidizing agents are brought into contact with powerful reducing agents the reaction between them may be of great velocity, much heat may be generated, and, if any of the products be gaseous, explosion may be the result. Should inflammable gases be formed, the high temperature produced by the reaction may be sufficient to ignite them.

Explosions of gun powder, dynamite, gun cotton and other "explosives" are reactions of oxidation and reduction accompanied by the generation of intense heat, the sudden formation of large volumes of gases, and the appearance of flame from the combustion of one or more of the products.

**381.** The *oxidizing agent and the reducing agent* are, of

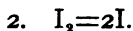
course, both contained in the *factors* of the reaction. They may be:

1. Different uncombined atoms of the same element.
2. Different atoms of the same element combined with each other in elemental molecules.
3. Atoms of the same element contained in separate molecules of one kind.
4. Different uncombined elements.
5. Different elements contained together in the same compound molecule.
6. Different atoms of the same element contained in different compound molecules.
7. Atoms of different elements contained in different compound molecules.

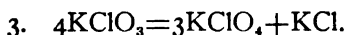
These several conditions, in the order mentioned, are illustrated by the following examples:



In this example ten chlorine atoms are reduced and the other two chlorine atoms are oxidized. The 10 chlorine atoms which were reduced lost together 10 units of polarity-value; while the two that were oxidized gained together the same number. The Cl in  $\text{CaCl}_2$  has a polarity-value of  $-1$ ; but the Cl in chlorates has a polarity-value of  $+5$ . But 10 chlorine atoms *gained 1 bond* each, and the other two gained 5 bonds each.

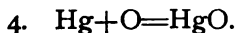


In all diatomic molecules one atom is positive and the other negative. When diatomic molecules of iodine are split up by heat into monatomic molecules, the positive iodine atom of the molecule  $\text{I}_2$  loses one unit of polarity-value while the negative iodine atom gains one unit, for both atoms when separated from each other acquire a polarity-value of 0. Both atoms lost 1 bond each.

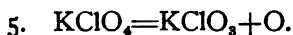


Here the Cl in  $\text{KClO}_3$  has a polarity-value of  $+5$ ; in  $\text{KClO}_4$  the Cl has a polarity-value of  $+7$ ; and the Cl in  $\text{KCl}$  has a value of  $-1$ . The three chlorine atoms of three molecules of  $\text{KClO}_3$  gained 2 units each, or 6 units together, and these 6 units were all lost by the single chlorine atom in the fourth molecule of

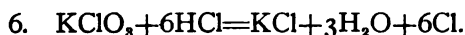
$\text{KClO}_3$  for that atom had its polarity-value reduced from  $+5$  to  $-1$ . But while three chlorine atoms gained together 6 bonds, the fourth atom lost 4 bonds.



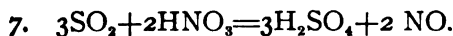
Here the O is the oxidizing agent and the Hg is the reducing agent. Two units of polarity-value are given up by the O and acquired by the Hg.



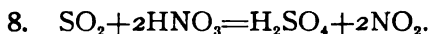
Here the chlorine atom of the  $\text{KClO}_4$  is the oxidizing agent and one of the oxygen atoms of the same molecule is the reducing agent, for the chlorine atom loses 2 units of polarity-value and the oxygen atom receives them. The polarity-value of the Cl is reduced from  $+7$  to  $+5$ ; that of the oxygen is increased from  $-2$  to 0, for it lost its two negative bonds.



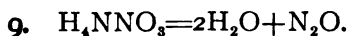
The chlorine atom of the  $\text{KClO}_3$  loses 6 units of polarity-value, being reduced from a polarity-value of  $+5$  to one of  $-1$ . These 6 units are transferred to the six chlorine atoms of the six molecules of HCl, which assume a polarity-value of 0 when liberated.



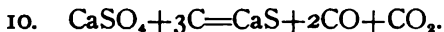
Here the S of the  $\text{SO}_2$  has a polarity-value of  $+4$ , which rises to  $+6$  in the  $\text{H}_2\text{SO}_4$ ; each sulphur atom therefore gains 2 positive bonds, so that the three sulphur atoms of the three molecules of  $\text{SO}_2$  together gain 6 positive bonds, all of which are taken from the two nitrogen atoms of the two molecules of  $\text{HNO}_3$ , for the N in  $\text{HNO}_3$  has a polarity-value of  $+5$  whereas the N in NO has a value of  $+2$ , each nitrogen atom, therefore, losing 3 positive bonds.



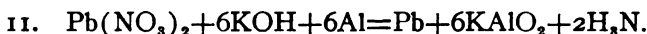
Here each nitrogen atom loses only 1 bond, and the sulphur atom gains 2.



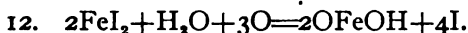
Here one nitrogen atom gained 4 units of polarity-value and the other lost them; but both lost 4 bonds each.



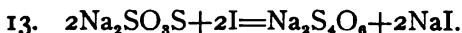
Here the S is the oxidizing agent and C the reducing agent; but the C acquires a polarity-value of +2 in CO and of +4 in CO<sub>2</sub>.



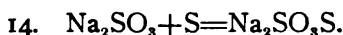
Both the Pb and the N of the Pb(NO<sub>3</sub>)<sub>2</sub> lose units of polarity-value which are taken up by the Al.



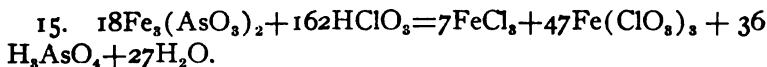
Both the iron and the iodine of the FeI<sub>2</sub> gain increased polarity-value at the expense of the oxygen.



Here only one of the four sulphur atoms of the two molecules of Na<sub>2</sub>SO<sub>3</sub>S is oxidized, taking up the units of polarity-value lost by the 2I.



Here the S of the Na<sub>2</sub>SO<sub>3</sub> gained 2 positive bonds which were furnished by the uncombined sulphur which acquired a polarity-value of -2 in the Na<sub>2</sub>SO<sub>3</sub>S.



In this reaction both the iron and the arsenic of the Fe<sub>3</sub>(AsO<sub>3</sub>)<sub>2</sub> acquired additional units of polarity-value at the expense of the Cl of 21 of the molecules of HClO<sub>3</sub>.

**382.** The *products* of reactions of oxidation and reduction may be either atoms or molecules, or both; they may be elemental or compound molecules, or both; and the atoms whose polarity-value has been increased or diminished may, if combined, be contained in different molecules of one kind, or in different molecules of different kinds, or in one and the same molecule.

**383.** Units of positive and negative polarity-value are, like

matter and energy, uncreatable and indestructible. They can only be transferred from one element to another, and from one atom to another of the same element. Hence polarity and valence are not forms of chemical energy for they can not be converted into other forms of energy. The high polarity-value exercised by the most powerful oxidizing agents known must therefore have been derived from other oxidizing agents furnishing an inexhaustible store which is replenished as rapidly as drawn upon.

The oxygen of the air is the never-failing oxidizing agent by means of which all other important oxidizing agents are produced. The motive of this oxidation through the agency of the oxygen of the air is to be found partly in the determining or pre-disposing affinities of strong bases and acids. It is frequently aided by the greater energy of elements in the atomic condition or *nascent state*.

Ozone is a most powerful oxidizing agent because it is easily split up into ordinary diatomic molecules of oxygen and nascent (atomic) oxygen. Hydrogen dioxide is another exceedingly effective oxidizing agent, being split up into water and nascent oxygen. And free chlorine acts as a powerful oxidizing agent toward numerous compounds containing hydrogen and oxygen directly united to each other, because the chlorine appropriates to itself the hydrogen and thus disconnects the oxygen bonds, and in taking the hydrogen from water associated with certain compounds it produces nascent oxygen.

(See also Chapter XXI.)

**Oxidizing agents and reducing agents are always atoms, either free or in combination. Nevertheless it is customary and convenient to designate as oxidizing agents and reducing agents all molecules containing the atoms reduced or oxidized, and this is permissible provided the student always has clearly in mind the fact that only atoms can gain or lose units of polarity-value.**

## CHAPTER XIX.

### THE FORCES AND CONDITIONS WHICH DOMINATE THE COURSE OF CHEMICAL REACTIONS.

**384.** Although chemical combination and all rearrangements of atomic linking are ever determined by chemism, yet the initiative of chemical action may be some other form of energy, and the direction, velocity and extent of chemical reactions depend upon both physical and chemical conditions.

Chemical interchange and what has been termed "selective affinity" must necessarily depend chiefly upon the composition of the molecules concerned; but heat, light, cohesion and adhesion, the relative masses of reacting molecules and the freedom of contact between them, and the removal of the products from the arena of chemical action—all have great influence upon the results.

**385.** The influence of **heat** upon matter is generally in opposition to atomic as well as molecular attraction.

It seems probable that at a sufficiently intense heat all molecules would be disrupted and matter reduced to the atomic state; but no such high temperature is attainable.

On the other hand a sufficiently low temperature would probably arrest all molecular motion; but such intense cold is also unattainable.

**386.** Chemical *decomposition* is attended by the absorption of heat; whereas chemical *combination* results in the liberation of heat.

The amount of heat motion started in the formation of a compound from its component elements is exactly the same as the amount of heat required to decompose the same compound.

But chemical energy manifests itself as a form of attraction while thermal energy is repellent.

**387.** Chemical reactions tend toward the production of the largest proportion of thermal energy, so that when several different reactions are each possible between any given kinds of matter the particular reaction which will actually take place may be determined by that tendency.

**388.** Heat is very frequently employed to induce or facilitate chemical reactions, and the most familiar illustration of this is furnished by the combustion of fuel *to produce heat*. A certain amount of heat is necessary to start the combustion, after which the chemical combinations which take place in that combustion evolve thermal energy more than sufficient to maintain it.

Heat aids or starts chemical action mainly by causing the decomposition of existing molecules and thus clearing the way for the rearrangement of the dissociated atoms or groups of atoms into new molecules.

But there are apparent exceptions to the general rule just given, for heat may cause free elements to combine, and, when the temperature is raised higher, may cause the compounds thus formed to decompose again. This is seen in the formation of mercuric oxide by heating the metal in air at a temperature a little below the boiling point, which is about  $357^{\circ}$  and the decomposition of the oxide when heated to glowing.

The different effects of different temperatures upon compounds is illustrated by the fact that barium oxide,  $\text{BaO}$ , when heated in air, takes up more oxygen and forms barium dioxide,  $\text{BaO}_2$ , while the dioxide decomposes at a higher temperature, giving up one-half of its oxygen and is thus converted into the lower oxide,  $\text{BaO}$ , again.

**389.** Light, too, has great chemical influence upon numerous kinds of matter. Like heat it causes decomposition rather than chemical union.

Instantaneous photography illustrates in a most striking manner the power of light to cause chemical changes.

The decoloration and discoloration of many substances by the action of light, the decomposition of certain compounds of silver and of mercury by it, and its destructive effects upon alkaloids, volatile oils, and numerous other valuable substances, attest the decided influence which light exerts upon the constitution of matter.

**390.** It has already been pointed out elsewhere in this book that *electrical energy* may be produced by chemical action, and also that chemical decomposition by means of electricity, called electrolysis, may be effected in certain compounds called electrolytes.

**391.** As heat, light and electricity are different forms of en-

ergy causing molecular motion, and as each would seem to cause chemical decomposition, it is apparent that molecular motion directly affects atomic motion which is caused by the chemical form of energy.

**392.** The chemical laws and conditions which determine chemical reactions have direct reference to the relative stability of factors and products, and to the energy, selective affinity, polarity, and valence of the radicals involved.

The fact has already been mentioned that certain elements or families of elements have a more decided inclination to enter into chemical combination than others.

It has also been stated that only elements assuming opposite polarity unite, that elements of low valence generally exhibit greater chemical energy than those of higher valence, and that atoms in the nascent state are more energetic chemical agents than matter in a molecular condition.

In reactions of oxidation and reduction it is seen that molecules containing elements having a low polarity-value, but capable of oxidation, react readily with molecules containing elements having a high polarity-value capable of reduction, with the result that products are formed in which the oxidizing agent and the reducing agent exhibit a diminished difference in polarity-value, provided always that the formation of such products be consistent with the affinities of the other elements contained in the factors.

One of the two nitrogen atoms of ammonium nitrate,  $\text{H}_4\text{NNO}_3$ , has a polarity-value of  $-3$  and the other a polarity-value of  $+5$ . When this salt is decomposed by heat the products are  $\text{N}_2\text{O}$  and water. Both of the nitrogen atoms, therefore, then assume a polarity-value of  $+1$ , four units of polarity-value having been transferred from one to the other by the reaction.

But the opposite result may be seen in some instances, as when potassium chlorate is decomposed by heat into chloride and perchlorate. The chlorine in potassium chlorate,  $\text{KClO}_3$ , has a polarity-value of  $+5$ . The reaction is represented as follows:



Here the chlorine which forms the perchlorate assumes a higher polarity-value than it had before, while the chlorine forming the chloride is reduced to a polarity-value of  $-1$ . This result is due to

the fact that negative chlorine is a much more powerful negative radical than  $\text{ClO}_3$  and the strongly basic potassium predisposes the reaction so that the very stable molecule  $\text{KCl}$  is formed while the nascent oxygen liberated by the dissociation causes the formation of  $\text{KClO}_4$  out of three molecules of the  $\text{KClO}_3$ .

Thus it is seen that the various physical and chemical influences which affect chemical reactions may operate in different directions, or in opposition to each other, rendering a correct prognosis of the net result quite difficult in some instances.

**393. Malaguti's doctrine.** The chemist Malaguti formulated the doctrine that in metathetical reactions, by which so many inorganic salts are produced, the strongest acid tends to combine with the strongest base.

This doctrine, applied to all kinds of chemical reactions, may be expressed as follows in conformity to modern chemical views:

**Chemical reactions are subject to a tendency toward the pairing of the strongest radicals of opposite polarity.**

The strongest positive radical present has a tendency to unite with the strongest negative radical present, and the rearrangements of atomic linking caused by the tendency toward the pairing of the strongest radicals of opposite polarity may be more complex than simple metathesis.

The underlying cause is clearly the universal tendency of matter to form molecules of the greatest degree of stability under the conditions obtaining at the time of their formation.

But when more than one product is formed by the reaction and one of them is composed of the strongest radicals of opposite polarity, the other product or products must be composed of less powerful radicals and must be less stable.

Moreover, the pairing of the strongest radicals of opposite polarity is frequently interfered with, opposed, or even completely nullified by other laws or conditions.

**394.** The common observation that stronger acids have the power to decompose the salts of weaker acids, and that stronger bases show a tendency to decompose the salts of weaker bases, attests the correctness of Malaguti's doctrine.

Experimental investigations of the effects of acids upon salts have led to the conclusion that hydrochloric acid is the strongest of the common acids, with nitric acid next in order, and that sulphuric acid is weaker than either of those two.

But when acids and salts are mixed in water-solutions and the extent of the resulting reactions measured, there are many conditions affecting the chemical equilibrium between the several molecules present. Among these conditions are the temperature, mass, solubility, density, volatility and other properties of the factors and products, the thermal energy produced, etc.

On the basis of their power of taking a metal from its chloride the following named acids have been assigned the relative positions here given:

Hydrochloric acid.  
Nitric acid.  
Hydrobromic acid.  
Sulphuric acid.  
Phosphoric acid.  
Silicic acid.

Experience shows, however, that sulphuric acid decomposes chlorides, bromides and nitrates as well as phosphates, and either phosphoric acid, boric acid, or silicic acid, although they have no effect upon sulphates under ordinary conditions, will decompose the sulphates at a very high heat, because sulphuric acid is less volatile than hydrochloric acid, nitric acid, or hydrobromic acid, but more volatile than boric acid, while phosphoric acid and silicic acid are not volatile at all.

Under the ordinary conditions obtaining in pharmaceutical laboratory work, the order in which the acids apparently stand to each other as to their power to decompose each other's salts, or to displace each other, would seem to be different from that assigned them in the preceding table based upon experiments conducted under different conditions.

A few of the most common acids may be mentioned in the following order according to their power to decompose each other's salts under ordinary conditions:

Sulphuric acid.  
Nitric acid.  
Hydrochloric acid.  
Hydrobromic acid.  
Phosphoric acid.  
Oxalic acid.

Tartaric acid.

Citric acid.

Acetic acid.

Carbonic acid.

**395.** Of the common bases potassium hydroxide is the most powerful. It, therefore, tends to decompose the salts of all other metals, except rubidium and cæsium. Sodium hydroxide has a tendency to decompose the salts of all metals except potassium, rubidium and cæsium. Either of the alkali bases have the disposition to decompose the salts of the alkaline-earth metals, earth metals, and heavy metals.

Nearly all metals have the power to displace hydrogen from the acids.

**396.** In accordance with the doctrine of Malaguti we should expect such reactions as the following:

1.  $2\text{KC}_2\text{H}_3\text{O}_2 + \text{Cu}(\text{NO}_3)_2 = 2\text{KNO}_3 + \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ .
2.  $\text{KBr} + \text{HCl} = \text{KCl} + \text{HBr}$ .
3.  $\text{Na}_2\text{HPO}_4 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{H}_3\text{PO}_4$ .
4.  $\text{Na}_2\text{CO}_3 + 2\text{HCl} = 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$ .
5.  $\text{K}_2\text{C}_4\text{H}_4\text{O}_6 - \text{MgSO}_4 = \text{K}_2\text{SO}_4 + \text{MgC}_4\text{H}_4\text{O}_6$ .

The principal reactions in which the doctrine of Malaguti operates to any great extent without the aid of other influences are metatheses between water-soluble substances in a state of solution in water, resulting in the formation of water-soluble products. But such reactions are never complete on account of the interference caused by the influence of the relative masses of factors and products in contact with each other, because the products are not removed from the "arena of chemical action."

Potassium acetate and copper nitrate are both water-soluble. When solutions of these two salts are mixed there is a reaction between them according to the law that potassium, the strongest of the two positive radicals, is disposed to unite with the nitrate radical which is the most powerful of the two negative radicals. But, as the potassium nitrate and copper acetate are also water-soluble, the reaction does not proceed to completion and the solution will contain four salts instead of two—the nitrates of potassium and copper and the acetates of copper and potassium.

Potassium bromide and hydrochloric acid in water-solution do not form potassium chloride and hydrobromic acid to the exclusion of remainders of the factors, because the chlorides and bromides of potassium and hydrogen are all water-soluble and remain in the liquid.

Sodium is a more powerful positive radical than hydrogen and the sulphate radical is a stronger negative radical than the phosphoric-acid-residue. Hence, according to the doctrine of Malaguti, sodium phosphate and sulphuric acid ought to produce sodium sulphate and phosphoric acid; but the reaction is not complete for both factors and products are soluble and remain in the liquid.

Potassium tartrate and magnesium sulphate in solution together should form potassium sulphate and magnesium tartrate, and these products are, indeed, formed; but the reaction is arrested while considerable quantities of the factors still remain undecomposed, because both factors and products remain dissolved in the liquid.

Sodium carbonate and hydrochloric acid should form sodium chloride and carbonic acid in obedience to Malaguti's law; and the reaction does result in those products because the carbonic acid decomposes into water and carbon dioxide, and the latter *passes off*.

**397.** Intimately connected with the relative intensity of the chemical energy of the radicals composing the reacting molecules is that condition which is termed the *status nascendi*.

This is a potent factor in certain reactions.

Gold does not dissolve as readily in an "aqua regia" in which all reaction between the acids has ceased and no more chlorine is being liberated as it does in hydrochloric acid to which the nitric acid is gradually added so that the gold is attacked by *nascent chlorine*.

And the same principle applies to compound radicals as well as to the elemental radicals. A mixture of sodium acetate, sulphuric acid and alcohol forms ethyl acetate more readily than absolute acetic acid and alcohol; a mixture of potassium nitrate and sulphuric acid attacks cotton more vigorously than nitric acid does; and amyl valerate is best prepared from amyl alcohol, sodium valerate and sulphuric acid rather than from amyl alcohol and valeric acid.

**398. Predisposing affinity.** Chemical reactions are frequently induced between two factors through the mediation of a third factor in cases where no reaction would take place in the absence of such mediation. This result is apparently attributable to the predisposing affinity between one of the radicals of the third factor and one of the radicals of a product formed by the other two factors.

In such cases there are frequently two or more reactions in succession.

A and B may not react upon each other in the absence of other substances, but may do so in the presence of C, provided that C reacts readily with one of the products of the *primary reaction* between A and B.

A relatively powerful positive radical may thus determine or predispose the formation of a negative radical with which it may combine, and vice versa, the final result being a relatively stable molecule.

Aldehyde in alcoholic solution is not readily oxidized to acetic acid by reaction with the oxygen of the air; but potassium acetate is rapidly formed if some potassium carbonate be added to the solution, and that, too, notwithstanding the fact that the carbonate is insoluble in alcohol.

The corrosive action of common strong sulphuric acid upon wood and other organic substances is chiefly due to the avidity of that acid for water with which it reacts to form mono-meta-sulphuric acid and normal sulphuric acid. This predisposing affinity of the di-meta-sulphuric acid for water compels the decomposition of the organic matter that water may be formed with which the acid may then react, or the ordinary sulphuric acid abstracts the hydrogen and oxygen separately and directly.

The formation of oxalic acid by the action of potassium hydroxide upon sawdust is aided if not produced by predisposing affinity, the product being potassium oxalate.

In certain chemical reactions accompanied by changes of the polarity-values of one or more of the elements constituting or contained in the factors, the cause of the transfer of units of polarity-value is predisposing affinity which brings about a rearrangement of the atoms such as results in the formation of powerful radicals out of the building materials at hand in order that the final products may be relatively stable compounds.

Strong acids coming in contact with metallic compounds in which the metals have a higher valence than they can retain when exercising basic functions, often reduce the polarity-value of the metals in order to form salts.

Certain very weak acids are known only through their salts with the strongest bases.

That oxidation depends largely upon predisposing affinity may be seen from the following examples:

1. Potassium nitrate may be produced out of the ammonia liberated from urine and certain other animal substances containing nitrogen compounds. The nitrogen of this ammonia is oxidized, at the expense of the oxygen of the air, from a polarity-value of  $-3$  to one of  $+5$  in the formation of the saltpetre. But this result is rendered possible only by the presence of the strong base which forms the nitrate. A mixture of earth and wood ashes with alternating layers of twigs for the purpose of admitting air, is moistened from time to time with urine, blood, etc. The potassium carbonate of the wood ashes then causes the formation of potassium nitrate.

2. Manganese dioxide,  $\text{MnO}_2$ , occurs in nature. Its manganese atom has a polarity-value of  $+4$ . When it is heated with acids it forms manganous salts in which the metal has a polarity-value of  $+2$ ; but when heated with potassium hydroxide the  $\text{MnO}_2$  forms potassium manganate,  $\text{K}_2\text{MnO}_4$  in which the manganese has a polarity-value of  $+6$ . When potassium manganate is boiled in water, it decomposes as follows:



Hence we see that the manganese of two molecules of the  $\text{K}_2\text{MnO}_4$  gained two positive bonds while the manganese of the third molecule of  $\text{K}_2\text{MnO}_4$  lost two positive bonds in forming the insoluble  $\text{MnO}_2$ . Moreover, the decomposition of the  $\text{K}_2\text{MnO}_4$  in water-solution with the formation of permanganate,  $\text{KMnO}_4$ , and manganese dioxide,  $\text{MnO}_2$ , is greatly facilitated by passing carbon dioxide through the solution whereby  $\text{K}_2\text{CO}_3$  is formed instead of  $\text{KOH}$ .

3. Potassium chlorate is formed by the action of chlorine upon potassium hydroxide because potassium chloride is formed at the same time, and because the oxygen which is detached from the potassium hydroxide is, in its nascent state, able to form the

chlorate with the aid of the predisposing affinity of potassium for all acids.

4. Chromous compounds contain bivalent chromium. They are oxidized in the air, *in the presence of acids*, to chromic salts in which the chromium is trivalent; but *in the presence of strong bases* the chromous compounds are oxidized by the oxygen of the air to chromates in which the chromium exercises a polarity-value of  $+6$ . Dilute acids remove one-half of the potassium from potassium chromate, converting it into dichromate (a meta-salt), which is a commonly employed and efficient oxidizing agent.

(See also par. 392.)

**399.** The **physical conditions** most favorable to satisfactory results in chemical reactions concern both factors and products.

With reference to the *factors* it is important that the condition of cohesion (or "state of aggregation") shall be such as to admit of sufficient freedom of motion of the molecules to insure immediate and free contact, but not such a nullification of molecular attraction as would result in dispersion, and the relative masses of the factors must be definite and favorable to as complete reactions as can be effected.

**400.** *Solids* do not readily react upon each other, or upon liquids or gases.

*Liquids* react most readily and completely.

*Gases* react more freely than solids, but the gaseous condition is less favorable than the liquid.

*Solids and solids* may be made to react upon each other only in very few instances, and the results are rarely satisfactory because it is impossible to bring solid substances into immediate contact throughout their masses even if they be triturated together under strong pressure. Such reactions are slow and incomplete. Better results are obtained when the solids are liquefied by fusion or solution whenever such liquefaction is practicable.

*Solids react with liquids* much more readily than solids with other solids. Such reactions are often employed in the production of chemical compounds.

Reactions between *solids and gases* occur, but are generally incomplete and not often of practical value.

Reactions between *gases and gases* seldom afford a satisfactory outcome in the problems of industrial and pharmaceutical chemistry.

Reactions between *liquids and gases* are frequently utilized with satisfactory results.

But chemical reactions between *liquids and liquids* proceed most advantageously and are employed to a far greater extent than all the others together. Reactions between factors in a state of *solution* in water are promptly effected because acids, bases and salts in water-solution are in a state of dissociation into their respective ions, i. e., into their respective positive and negative radicals. (See Chapter VI.)

**401.** Reactions between fusible substances which are solids at the ordinary temperature may be induced by the application of heat sufficient to cause fusion whereby free contact between them is facilitated; but satisfactory results are rarely attainable unless one of the products be fusible and the other infusible at the temperature of the reaction, or one of the products gaseous and the other either liquid or solid.

A synthesis between two factors in the solid state may be effected by fusion if the one product formed is fusible.

**402.** Reactions between infusible solids are scarcely practicable unless one of the factors be gaseous at the temperature of the reaction while the other is non-volatile.

Dissociation of solid substances is practicable only in cases where at least one of the products is a gas.

**403.** The direction, velocity and relative completeness of chemical reactions are frequently dominated by the separability of the products from each other and from the factors.

Whatever impedes free contact between the factors in any chemical reaction impedes the reaction itself, or may arrest it or altogether prevent it.

Hence *chemical reactions are greatly facilitated by the removal of one or more of the products as rapidly as formed.*

**404.** If the products be two the reaction will be found to progress most satisfactorily: 1, If one be gaseous and the other either liquid or solid; or 2, if one be a soluble substance and the other insoluble; or 3, if one of the products be a liquid and the other a solid insoluble in that liquid; or 4, if one of the products be water.

**405.** Berthollets doctrine of the formation of volatile products is to the effect that—

*Whenever the formation of a volatile (or gaseous) product is*

*possible at the temperature at which the reaction occurs, then the course of the reaction will be determined thereby and that volatile product will be formed.*

The following proposition would seem to be preferable:

*Chemical reactions are facilitated and rendered more complete when one or more of their products are gases.*

Calcium carbonate can be decomposed by heat because one of the products is the gas  $\text{CO}_2$ ; but pyro-phosphates and borates resist dissociation because they can not yield volatile products.

When ammonium chloride and calcium oxide are heated together the products are calcium chloride, water and ammonia.

Mercuric sulphate and sodium chloride form mercuric chloride and sodium sulphate if heated together at a temperature sufficiently high to vaporize the mercuric chloride.

**406.** Two solids, both insoluble in water, or nearly so, may nevertheless react upon each other *in water* provided the product formed be one and water-soluble.

Iron and iodine do not react upon each other uniformly or satisfactorily in their dry condition; but when placed in contact under water they readily react and form ferrous iodide because that compound is freely water-soluble.

Lead and iodine do not act freely upon each other either in or out of water because lead iodide is practically insoluble.

**407.** When one of the factors is a solid and the other a liquid the reaction rarely proceeds unless one of the products be soluble in the liquid while the other or others must be either water, or a gas, or both.

Reaction between a solid and a liquid is rarely complete if one of the products be an insoluble solid.

In the process called *chemical solution* the product must be soluble in the liquid in which the reaction is effected.

Acids do not dissolve metals unless they form with them salts which are soluble in the acid or in the water holding the acid in solution.

The chemical action of certain acids upon certain metals is only superficial on account of the insolubility of the metallic product formed.

Concentrated nitric acid is not acted upon by iron because nitrate of iron is not soluble in concentrated nitric acid; but iron

does act upon dilute nitric acid rapidly because iron nitrate is readily soluble in dilute nitric acid as well as in water.

Concentrated sulphuric acid is decomposed by lead because lead sulphate is soluble in concentrated sulphuric acid; but a somewhat dilute sulphuric acid may be allowed to come in contact with lead without any danger that the acid will be attacked by the metal, for lead sulphate is insoluble in dilute sulphuric acid as well as in water.

Moderately diluted nitric acid reacts more satisfactorily with silver than a stronger nitric acid because silver nitrate is far more readily soluble in water and in dilute nitric acid than in a stronger acid.

The bye-products in these reactions are gases and water.

**408. Berthollett's doctrine of the formation of insoluble products** is as follows:

*Whenever the formation of an insoluble product is possible in any reaction occurring in a liquid, that insoluble product will be formed;*

*Or, whenever, by any double decomposition between compounds in solution, an insoluble or less soluble compound can be formed, then that insoluble or less soluble compound will be formed;*

*Or, chemical reactions between substances in a state of solution are facilitated and proceed to completion when one of the products is insoluble or only sparingly soluble in the liquid.*

There is no exception to this rule. It nullifies or overcomes the tendency toward the union of the strongest radicals of opposite polarity in every case where Malaguti's law and this law of the formation of insoluble compounds operate in opposite directions.

When the product formed in obedience to this law is only less soluble than either of the factors, but not insoluble, the reaction may not proceed to completion; but whenever the product is quite insoluble in the liquid in which the reaction takes place, then the reaction will result in the complete decomposition of at least one of the reacting substances if proper proportions of the factors are employed.

Insoluble pharmaceutical chemicals are accordingly most frequently produced by metatheses between water-soluble factors.

A knowledge of the solubilities of chemical compounds in the common simple solvents, especially in water, and a knowledge of

what compounds are insoluble, therefore, afford the basis for practical methods of preparation of nearly all the insoluble salts and many other insoluble compounds producible by metathetic reactions.

Since lead iodide is practically insoluble in cold water, it follows that when a cold water-solution of any soluble lead salt is mixed with a cold aqueous solution of any iodide, a precipitate of the iodide of lead must be the inevitable result.

A water-solution of mercuric chloride when mixed with a water-solution of potassium iodide produces mercuric iodide and potassium chloride because mercuric iodide is insoluble (or nearly so).

To know that the oxides, hydroxides, sulphides, carbonates, oxalates, and phosphates of the heavy metals are all insoluble in water is to know that solutions of the water-soluble salts of those metals can not be mixed with solutions of any of the soluble hydroxides, sulphides, carbonates, oxalates or phosphates without producing precipitates.

Quinine salicylate is soluble in alcohol but insoluble in water. Sodium chloride is soluble in water but insoluble in alcohol. Sodium salicylate and quinine hydrochloride are both soluble in either alcohol or water. Now, if water-solutions of sodium salicylate and quinine hydrochloride be mixed with each other, the metathesis will produce sodium chloride which remains in solution and quinine salicylate which precipitates; if alcoholic solutions of the same factors be mixed, the same products will be formed, but then the sodium chloride will precipitate while the quinine salicylate remains dissolved in the liquid (alcohol).

**409.** The reactions depended upon for the identification and separation of elements and their compounds, or the reactions utilized in qualitative and quantitative analytical chemistry, are to a very great extent precipitations formed in obedience to the law of the formation of insoluble compounds by metathesis.

**410.** The **relative proportions or masses** of the factors in any chemical reaction affect the results very materially.

It must be understood, in this connection, that by "relative proportions" or "relative masses" is meant *the relative number of molecules*.

Since the elements combine in definite proportions according to simple multiples of their atomic weights, it follows that the

factors of any chemical reaction must be taken in definite proportions according to their molecular weights and the number of molecules required of each to produce a complete interchange such as shall leave no remainder of either of the factors.

But experience has shown that the exact proportions required by theory do not as a rule result in the complete decomposition of the several factors.

On the other hand, it has been found that when one factor is present in very decided excess over the other a reaction may be caused between two substances which do not react upon each other to the same extent, if at all, when the proportions employed are those actually taking part in the atomic interchanges.

When iron is dissolved in hydrochloric acid the action is at first comparatively rapid because the acid coming into actual contact with the iron is a relatively large proportion; but as the reaction progresses the acid forms ferrous chloride and as the quantity of acid remaining in the liquid is thereby diminished the velocity of the reaction gradually decreases. Not only the presence of the iron chloride but also the decreasing proportion of acid retards the chemical action.

When barium sulphate, which is insoluble in water, is acted upon by a solution of sodium carbonate, portions of the two salts are decomposed so that the solution will contain both sodium sulphate and sodium carbonate while the insoluble solid matter will become a mixture of barium carbonate and barium sulphate. But this double decomposition soon ceases unless the solution of sodium salts be removed from time to time and replaced by fresh portions of solution of sodium carbonate. Repeated treatment with fresh portions of sodium carbonate will, however, finally convert the whole quantity of barium sulphate into barium carbonate.

The fact should not be lost sight of that sodium is a stronger positive radical than barium, and that the formation of sodium sulphate and barium carbonate from sodium carbonate and barium sulphate is in accord with the doctrine of Malaguti; but when sodium sulphate and barium acetate in water-solution are mixed in the proportions required for even or complete metathesis barium sulphate and sodium acetate are formed and the reaction proceeds to completion because the barium sulphate is insoluble.

The decomposition of the nitrate or sulphate of mercury, or of bismuth nitrate, or of antimony chloride, by large quantities of water must also be the result of the influence of greater mass, although, at the same time, the insolubility of the products has a decided bearing upon the final outcome. The composition of the insoluble product varies according to the relative mass of the water used, containing a larger percentage of metal when the amount of water is greater.

## CHAPTER XX.

### HOW TO WRITE AND BALANCE ORDINARY CHEMICAL EQUATIONS.

**411.** A **chemical equation** is an expression of a chemical reaction by means of the symbolic molecular formulas of its factors and products.

It is composed of two *members*. The *first member* of a chemical equation must show the kind and least relative number of each of the reacting molecules or factors; the *second member* must show the kind and number of the new molecules or products.

The two members of the equation are separated from each other by the usual "equal sign," or  $=$ ; the factors which together constitute the first member are separated from each other by the plus sign,  $+$ , and the products, which constitute the second member, must be separated from each other by the same sign.

**412.** When uncombined elements are referred to in chemical equations they may be represented either by their symbols, or by their molecular formulas if known. Both methods of expression are commonly employed. As matter exists only in a molecular form all the factors and products of a chemical reaction should, if possible, be written accordingly. But the molecular formulas of most of the elements are unknown, and it is also more convenient to write atoms instead of elemental molecules.

**413.** When the factors and products include substances of different "states of aggregation," or conditions of cohesion, the molecules of solids are usually written first and those of gases last. At the same time, so far as this order permits, that factor which supplies the positive radical of the principal product is placed at the beginning of the first member of the equation, and the principal product itself is written first in the second member of the equation.

**414.** When either the factors or the products, or any of them, contain chemically combined water, or water of crystallization, that water may be omitted from the molecular formulas except when chemical equations are written as a basis for stoichiometric calculations, when it is, of course, necessary to take into account the water contained in both materials and products.

**415.** In order to *balance* chemical equations it is necessary to know not only the correct molecular formulas of the reagents and products, but also the respective combining values and polarities of the radicals which change places in the reaction.

The kinds and numbers of the atoms entering into the molecules of the *factors* must be the same as in the *products*. Thus the total number of atoms in one member of the equation must be the same as in the other member of it; the number of atoms of any one kind must be the same in each member of the equation; any atom or atoms found on one side of the "equal sign" must also be found on the other side of it; every molecular formula must be complete; and no free or uncombined radical must be found in either member of the finished equation.

**416.** The correct *prognosis* of chemical reactions is generally practicable from a thorough knowledge of the laws of chemical composition and decomposition, and from the known influence of physical conditions upon the direction and extent of chemical action. These laws and conditions have been discussed in Chapter XIX. But it is sometimes impossible to predict with certainty from theory what products will be formed from the factors brought into reaction upon each other and in all such cases the known results of experience can be the only guide.

Complete and correct chemical equations can not be written without previous knowledge, from theory or practice, of what products will be formed (or at least what the principal product is); but if the factors and products are known the number of molecules of each may be readily found by "balancing the equation."

**417.** The objects of the employment of chemical equations are two: 1, To demonstrate the nature or rationale of the reaction; and 2, to determine the number of molecules required of the factors, and the number of molecules of the products obtained, respectively, in order that the proportions by weight of both factors and products may be computed accordingly from the molecular weights.

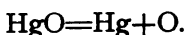
One of the most important requisites in devising and formulating a process for the production of a chemical compound is, therefore, the construction of the chemical equation which correctly indicates the materials required, the products and bye-products

obtained, and the quantities of each. The computation of these quantities is called *stoichiometry*.

418. It is clear that the equations representing reactions of **dissociation** are the most simple, since the first member of the equation consists of but one factor and the second member must consist of the molecules produced by splitting the molecule or molecules of the factor.

The following examples illustrate equations representing dissociation:

1. We know that when mercuric oxide is heated to redness it decomposes into mercury and oxygen. Hence we write:



That this equation balances is, of course, predetermined by the fact that the molecule HgO was simply divided into its component atoms Hg and O.

2. The dissociation of calcium carbonate by heat is known to result in the formation of calcium oxide and carbon dioxide. We, therefore, write:



3. We know that when potassium bicarbonate is heated at 100° C. it breaks up into potassium carbonate, water and carbon dioxide. We write down these molecules in the form of an equation, thus:

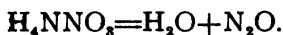


But when we examine this equation we find at once that its two members do not balance each other, for, in order to get one molecule of  $\text{K}_2\text{CO}_3$  we must have two molecules of  $\text{KHCO}_3$  since the former contains two potassium atoms and the latter only one. Our equation will then be balanced:

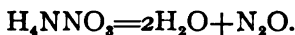


The student will find that all of the atoms in the two molecules of  $\text{KHCO}_3$  reappear in the products.

4. It is known that when ammonium nitrate is heated to a sufficiently high temperature dissociation results and that the products are  $\text{H}_2\text{O}$  and  $\text{N}_2\text{O}$ . We accordingly write:

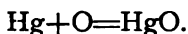


But when we count the atoms of hydrogen and oxygen in each of the two members of this equation it is seen that the first member contains 4 hydrogen atoms and 3 oxygen atoms while the products account for only 2 hydrogen atoms and 2 oxygen atoms. It is, therefore, evident that two molecules of water are formed instead of only one, and the equation, when balanced, accordingly will be:

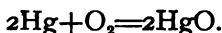


**419. Reactions of synthesis** are nearly as simple to write as those of dissociation, as will be seen from these examples:

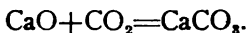
1. When mercury is heated in the air at a temperature somewhat below the boiling point of the metal, it is oxidized to mercuric oxide. If the mercury and oxygen be represented by their atoms the equation will be:



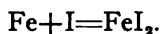
But if the reacting elements be represented by their molecules we shall have:



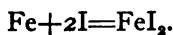
2. When calcium oxide is exposed to air containing carbon dioxide, the product of those two factors is calcium carbonate:



3. Iron and iodine put together under water unite to form ferrous iodide. To write the equation representing this reaction we can not use the molecular formulas of the factors because it is not known how many atoms are contained in the molecule of iron. Accordingly we write:



But we can see at a glance that this equation does not balance because we have only one atom of iodine on one side and two on the other; hence we must make the equation:

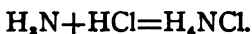


4. Calcium oxide and water react to form calcium hydroxide. When we write the molecular formulas of the factors and the product in the form of an equation we have:

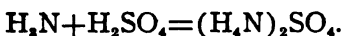


Upon examination we find that this equation is balanced and complete.

5. Ammonia and hydrochloric acid are known to form ammonium chloride:



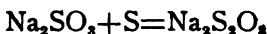
6. Ammonia and sulphuric acid form ammonium sulphate:



But this equation is not correct, for we find that we have 8 hydrogen atoms and 2 nitrogen atoms in the product, but only 5 hydrogen atoms and 1 nitrogen atom in the factors. Thus we require 2 molecules of ammonia in order to balance the equation:



7. Sodium sulphite and sulphur react with each other when boiled together in water and form sodium thiosulphate. When we use the molecular formulas of the sulphide and thiosulphate and the symbol for the atom of sulphur and write the equation:



we find that this equation is complete.

**420.** The most **simple metathetic reactions**—those of mutual interchange of radicals, or “double decomposition”—are easily represented by chemical equations because the same two positive radicals and two negative radicals composing the factors reappear unchanged in the products.

To balance equations representing reactions of double or mutual exchange of radicals it is only necessary to keep in view the fact that—

*The number of bonds or combining units presented by the positive radical of one of the factors must be the same as the*

*number of bonds or combining units presented by the positive radical of the second factor;*

*Or that the number of bonds or combining units presented by the negative radical of one of the factors must be the same as the number of bonds or combining units presented by the negative radical of the second factor.*

The sum of the bonds required of each of the two positive radicals of the factors (and of each of the two negative radicals of the factors) is usually the least common multiple of the numbers expressing their respective valences.

The following examples will suffice to illustrate this:

In a mutual exchange of radicals taking place between a sodium salt and a calcium salt, it is necessary to bear in mind that the sodium is a monad and the calcium a dyad so that in order to have the same number of sodium bonds as of calcium bonds we must multiply the number of sodium bonds in one molecule of the sodium salt by the number of calcium bonds in one molecule of the calcium salt in order to find the common multiple of the two numbers, and then we take such a number of molecules of each salt as will contain that number of sodium bonds and calcium bonds respectively:

1.  $\text{Na}_2\text{CO}_3 + \text{CaCl}_2 = 2\text{NaCl} + \text{CaCO}_3.$
2.  $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{NO}_3)_2 = 2\text{NaNO}_3 + \text{CaCO}_3.$
3.  $2\text{NaOH} + \text{CaCl}_2 = 2\text{NaCl} + \text{Ca}(\text{OH})_2.$
4.  $\text{Na}_2\text{HPO}_4 + \text{CaCl}_2 = 2\text{NaCl} + \text{CaHPO}_4.$
5.  $2\text{Na}_3\text{PO}_4 + 3\text{CaCl}_2 = 6\text{NaCl} + \text{Ca}_3(\text{PO}_4)_2.$

The student will find that in all of these equations the number of sodium bonds is the same as the number of calcium bonds in the factors and also in the products. In the first four equations there are 2 sodium bonds and 2 calcium bonds in both the factors and the products; and in the fifth equation there are 6 sodium bonds and 6 calcium bonds.

It will also be found that the bonds of the negative radicals are the same numbers.

**421.** When the positive radicals and the negative radicals of the two factors have, all of them, the same valence, then an equal

number of molecules of each, or one molecule of each, must be taken.

**422.** Further illustrations are furnished by the following equations in all of which the student will find that the number of bonds presented by the positive radical of the first factor is the same as the number presented by the negative radical of the same factor, and the same also as the number of bonds presented by the positive radical of the second factor, and by the negative radical of the second factor.

To facilitate the identification of the respective radicals the positive and negative radicals are separated by periods:

1.  $\text{Na.OH} + \text{H.NO}_3 = \text{Na.NO}_3 + \text{H.OH}.$
2.  $\text{H}_4\text{N.OH} + \text{H.NO}_3 = \text{H}_4\text{N.NO}_3 + \text{H.OH}.$
3.  $\text{Ag.NO}_3 + \text{Na.Cl} = \text{Ag.Cl} + \text{Na.NO}_3.$
4.  $\text{K}_2.\text{CO}_3 + \text{H}_2.\text{SO}_4 = \text{K}_2.\text{SO}_4 + \text{H}_2.\text{CO}_3.$
5.  $\text{Na}_2.\text{CO}_3 + \text{H}_2.\text{C}_4\text{H}_4\text{O}_6 = \text{Na}_2.\text{C}_4\text{H}_4\text{O}_6 + \text{H}_2.\text{CO}_3.$
6.  $2[\text{K.OH}] + \text{H}_2.\text{SO}_4 = \text{K}_2.\text{SO}_4 + 2[\text{H.OH}].$
7.  $\text{Pb.}(\text{NO}_3)_2 + \text{Cu.SO}_4 = \text{Pb.SO}_4 + \text{Cu.}(\text{NO}_3)_2.$
8.  $\text{Hg.O} + 2[\text{H.NO}_3] = \text{Hg.}(\text{NO}_3)_2 + \text{H}_2.\text{O}.$
9.  $\text{Pb.}(\text{NO}_3)_2 + 2[\text{K.I}] = \text{Pb.I}_2 + 2[\text{K.NO}_3].$
10.  $\text{Fe.}(\text{OH})_3 + 3[\text{H.NO}_3] = \text{Fe.}(\text{NO}_3)_3 + 3[\text{H.OH}].$
11.  $\text{Fe}_2.(\text{SO}_4)_3 + 6[\text{H}_4\text{N.OH}]$   
 $= 2[\text{Fe.}(\text{OH})_3] + 3[(\text{H}_4\text{N})_2.\text{SO}_4].$
12.  $\text{Na}_3.\text{C}_6\text{H}_5\text{O}_7 + \text{Bi.}(\text{NO}_3)_3 = \text{Bi.C}_6\text{H}_5\text{O}_7 + 3[\text{Na.NO}_3].$
13.  $\text{Fe.}(\text{OH})_3 + \text{H}_3.\text{C}_6\text{H}_5\text{O}_7 = \text{Fe.C}_6\text{H}_5\text{O}_7 + 6[\text{H.OH}].$
14.  $3[\text{Li}_2.\text{CO}_3] + 2[\text{H}_3.\text{C}_6\text{H}_5\text{O}_7] = 2[\text{Li}_3.\text{C}_6\text{H}_5\text{O}_7] + 3[\text{H}_2.\text{CO}_3].$
15.  $2[\text{KH.C}_4\text{H}_4\text{O}_6] + \text{K}_2.\text{CO}_3 = 2[\text{K}_2.\text{C}_4\text{H}_4\text{O}_6] + \text{H}_2.\text{CO}_3.$
16.  $\text{K}_2.\text{CO}_3 + \text{H}_2.\text{AsHO}_3 = \text{K}_2.\text{AsHO}_3 + \text{H}_2.\text{CO}_3.$
17.  $\text{Ca}_3.(\text{PO}_4)_2 + 4[\text{H.Cl}] = \text{CaH}_4.(\text{PO}_4)_2 + 2[\text{Ca.Cl}_2].$
18.  $\text{KNa.C}_4\text{H}_4\text{O}_6 + \text{H.Cl} = \text{KH.C}_4\text{H}_4\text{O}_6 + \text{Na.Cl}.$
19.  $\text{Bi.}(\text{NO}_3)_3 + 3[\text{Na.C}_7\text{H}_5\text{O}_3]$   
 $= \text{Bi.}(\text{C}_7\text{H}_5\text{O}_3)_3 + 3[\text{Na.NO}_3].$
20.  $2[\text{Al.}(\text{OH})_3] + 3[\text{H}_2.\text{SO}_4] = \text{Al}_2.(\text{SO}_4)_3 + 6[\text{H.OH}].$

**423.** Whenever carbonic acid,  $\text{H}_2\text{CO}_3$ , is a product it immediately splits up into water and carbon dioxide, so that the equations are generally written as if the latter products were directly formed. Water is generally written  $\text{H}_2\text{O}$  instead of  $\text{HOH}$ . Hence we write  $\text{K}_2\text{CO}_3 + \text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2$  instead of  $\text{K}_2\text{CO}_3 + \text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + \text{H}_2\text{CO}_3$ .

**424.** The following equations are less simple than those so far presented in this chapter; but the student is now prepared to understand them if those already studied are understood:

1.  $\text{As}_2\text{O}_3 + 4[\text{K.OH}] = 2[\text{K}_2\text{AsHO}_3] + \text{H}_2\text{O}.$
2.  $\text{As}_2\text{O}_3 + 2[\text{K}_2\text{CO}_3] + \text{H}_2\text{O} = 2[\text{K}_2\text{AsHO}_3] + 2\text{CO}_2.$
3.  $\text{As}_2\text{O}_3 + 3[\text{H}_2\text{O}] = 2[\text{H}_2\text{AsHO}_3].$
4.  $\text{CaH}(\text{PO}_4)_2 + 2\text{Ca.Cl}_2 + 4[\text{H}_4\text{N.OH}]$   
 $= \text{Ca}_3(\text{PO}_4)_2 + 4[\text{H}_4\text{N.Cl}] + 4[\text{H}_2\text{O}].$
5.  $2[\text{Bi}(\text{NO}_3)_3] + 3[\text{Na}_2\text{CO}_3]$   
 $= (\text{BiO})_2\text{CO}_3 + 6[\text{Na.NO}_3] + 2\text{CO}_2.$
6.  $\text{OBi.NO}_3 + \text{H}_3\text{C}_6\text{H}_5\text{O}_7 = \text{Bi.C}_6\text{H}_5\text{O}_7 + \text{H.NO}_3 + \text{H}_2\text{O}.$
7.  $4[\text{H}_4\text{N.Cl}] + 2[\text{Ca.CO}_3]$   
 $= 2[\text{Ca.Cl}_2] + \text{H}_4\text{NH.CO}_3 + \text{H}_4\text{N.H}_2\text{NCO}_2 + \text{H}_3\text{N} + \text{H}_2\text{O}.$
8.  $2[\text{FeH}_4\text{N}(\text{SO}_4)_2] + 6[\text{Na.PH}_2\text{O}_2]$   
 $= 2[\text{Fe}(\text{PH}_2\text{O}_2)_3] + 2[(\text{H}_4\text{N})_2\text{SO}_4] + 3[\text{Na}_2\text{SO}_4].$
9.  $\text{Fe}_2(\text{SO}_4)_3 + 2[\text{Na}_2\text{H.PO}_4] + 2[\text{Na.C}_2\text{H}_3\text{O}_2]$   
 $= 2[\text{Fe.PO}_4] + 3[\text{Na}_2\text{SO}_4] + 2[\text{H.C}_2\text{H}_3\text{O}_2].$

The student may now return to Chapters XIII and XVI and verify the correctness of the chemical equations given in paragraphs 315, 316, 355, 368, 369, 374, 375, and 381.

## CHAPTER XXI.

### HOW TO BALANCE EQUATIONS REPRESENTING REACTIONS OF OXIDATION AND REDUCTION.

**425.** A rule for balancing chemical equations attended by oxidation and reduction was suggested by Professor Otis C. Johnson of the University of Michigan, and his rule has been found to give correct results wherever applicable.

It was given in the following words in Prescott and Johnson's *Qualitative Chemical Analysis*:

"The number of bonds changed in one molecule of each shows the number of the molecules of the other which must be taken, the words *each* and *other* referring to the oxidizing and reducing agents."

This rule is based upon the fundamental fact that the increase of polarity-value gained by the reducing agent amounts to the same number of units as the diminution of polarity-value sustained by the oxidizing agent.

**The algebraic sum of the units of polarity-value of all atoms of all matter is always zero.** The total number of units of polarity-value transferred from the oxidizing agent to the reducing agent must accordingly be *the least common multiple of the number lost by the whole number of atoms of the oxidizing element or elements and the number gained by the whole number of atoms of the reducing element or elements.*

**426.** The procedure recommended in this book *for the purpose of finding the proportions required of the oxidizing agent and the reducing agent* preparatory to the balancing of chemical equations attended by oxidation and reduction is but an elaboration of Professor Otis C. Johnson's rule.

I. The factors and products of the reaction being known, write their molecular formulas (if compounds), or their symbols (if uncombined elements), in the form of an equation in the usual way (427).

II. Identify the oxidizing agent, or agents, and the reducing agent, or agents, among the factors (428).

III. Find the number of units of polarity-value lost by the oxi-

dizing agent and the number gained by the reducing agent (429). These numbers indicate the *proportions* required of the oxidizing and reducing agents to effect the oxidation and reduction (429).

IV. Add whatever additional molecules or atoms are requisite, if any, to balance the whole equation (430).

V. Balance the equation in the same manner as other chemical equations (not involving oxidation) are balanced (430).

VI. To finish the equation reduce it to its simplest terms, if requisite.

**427. Uncombined elements**, whether they be factors or products, are most conveniently represented by their symbols, or as free atoms instead of as elemental molecules.

If uncombined elements are represented by their molecules the operation of the rule is unnecessarily complicated by the fact that one-half of the tied bonds in any molecule consisting of more than one atom must be positive bonds and the other half negative bonds.

It will be shown further on that the rule gives correct results whether the uncombined elements which may enter into the equation be represented by their atoms or by their molecules.

**428. To identify the oxidizing agent and the reducing agent**, compare the polarity-values of the atoms *before* the reaction, as shown by the factors, with their polarity-values *after* the reaction, as shown by the products.

Any atom having a greater polarity-value before the reaction than after it is an oxidizing atom; and any atom found to have a greater polarity-value after the reaction than before is a reducing atom.

To determine the polarity-value of any atom it is necessary to have complete mastery of the principles laid down in Chapters IX and XVI and to know the polarity and valence of the most important elements in their common compounds (197).

The customary molecular formulas of the most common inorganic chemical compounds nearly always disclose the respective polarity-values of their component atoms at a glance, for the structure of inorganic compounds is generally very simple.

The polarity-value of the acidic element in any inorganic hydroxyl acid (as that of the chlorine in chloric acid, perchloric acid, chlorous acid or hypochlorous acid; that of the sulphur in sulphurous and sulphuric acid; that of the nitrogen in nitrous and nitric acid; etc.) is always a plus quantity, and, in any such acid,

containing only one atom of the acidic element in each molecule, it is found by deducting the total number of hydrogen atoms (or of hydrogen bonds) from the total number of oxygen bonds (or the doubled number of oxygen atoms).

Thus the polarity-value of the S in  $\text{H}_2\text{SO}_4$  is at once seen to be +6 because the bonds of that sulphur are positive bonds and their number is 6 because 2 from 8 leaves 6.

The polarity-value of the acidic element of any inorganic oxygen salt is found by deducting the total bonds of the basic element from the total oxygen bonds.

**429.** If the oxidizing agent and reducing agent are contained in compounds, note the number of units of polarity-value gained by the whole number of reducing atoms, contained *in one molecule*, which were oxidized by the reaction, and write that number before the oxidizing agent; and then note the number of units of polarity-value lost by the whole number of oxidizing atoms, contained *in one molecule*, which suffered reduction by the reaction, and write that number before the reducing agent.

But if the oxidizing agent and reducing agent, or either of them, be uncombined elements, note the number of units of polarity-value gained by each atom of the reducing agent and write that number before the oxidizing agent; then note the number of units of polarity-value lost by each atom of the oxidizing agent and place that number before the reducing agent.

These numbers are the respective co-efficients by which the oxidizing agent and reducing agent must be multiplied, and the least common multiple of these two numbers is necessarily either the total number of bonds transferred or a multiple of that total number.

The co-efficients referred to are but the proportions required to effect *the oxidation and reduction*, but are not always sufficient to complete and balance the whole equation as we shall soon see (430).

**430.** The molecules containing the atoms acting as oxidizing agents and reducing agents are often the only factors necessary. But whenever the numbers of molecules or atoms found requisite to effect the oxidation and reduction are not sufficient to complete the equation, the additional factors may be molecules or atoms of the same kinds, or other molecules, and the kinds and co-efficients of these additional factors may be readily discovered from

the products, after which the equation is easily balanced in the same manner as any equation in which no transfer of units of polarity-value takes place.

**431.** The total of the positive bonds in all of the *factors* of any correct chemical equation must be the same as the total of the positive bonds in all the *products*, *except in cases where the polarity of one or more atoms of any one element is reversed by the reaction*.

But if the bonds of any one or more atoms of one element suffer a reversal of polarity from positive to negative, and if the polarity of the same number of bonds of one or more atoms of another element be reversed in the opposite direction, then the two reversals of opposite polarities offset each other, and the total number of bonds of the atoms of all the molecules constituting one member of the equation will equal the total bonds of the atoms composing the molecules of the other member, as in all equations not attended by oxidation.

**432.** Whenever the oxidizing agent and the reducing agent are the same element in its free or uncombined state, one or more atoms of that element acting as the only oxidizing agent and another one or more atoms acting as the only reducing agent, these atoms reappearing in two of the products, the most convenient method of finding the number of atoms required of the oxidizing and reducing agent is as follows: Find the algebraic sum of the polarity-value of all the atoms of that element in one molecule of one of the products and the algebraic sum of all the atoms of the same element in one molecule of the other product; it will, of course, be found that this sum is in one of the products a plus quantity and in the other a minus quantity, since the oxidizing and reducing atom had a polarity-value of 0. As the number of units gained in one product must be the same as the number lost in the other product it follows that the number of molecules formed of each product must be governed by that fundamental law.

Examples illustrating this condition will be given further on (Ex. 65 to 73, par. 442).

See also par. 195 of Chapter IX.

**433.** The infallible working of the procedure described in this chapter for balancing all equations attended by "oxidation and reduction" (or transfers of units of polarity-value) proves

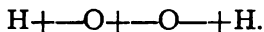
conclusively the existence of that condition which is represented by the expression "chemical polarity" and the all-pervading importance of its recognition in the solution of problems involving the structure of molecules and chemical interchanges between them.

434. The student is again warned against mistaking changes of ordinary valence for oxidation:

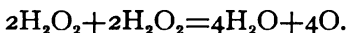


is an equation from which it is at once seen that the N in  $\text{H}_3\text{N}$  has a valence of 3, while the N in the product has a valence of 5; but the polarity-value of the N in both  $\text{H}_3\text{N}$  and  $\text{H}_4\text{NCl}$  is  $-3$ , and hence no oxidation attends this reaction.

2. In the equations  $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}$ , or  $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$ , or  $\text{BaO}_2 + \text{H}_3\text{PO}_4 = \text{BaHPO}_4 + \text{H}_2\text{O}_2$ , there is really no oxidation or reduction because the oxygen atoms of  $\text{H}_2\text{O}_2$  and  $\text{BaO}_2$  are united directly to each other, so that one of them has a polarity-value of  $-2$  and the other a polarity-value of 0, as shown here:



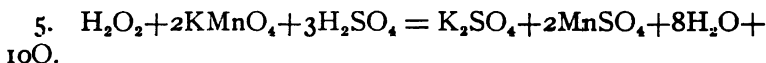
However, if you insist upon a literal application of the rule that we must take the algebraic sum of the units of polarity-value lost by all the atoms of the oxidizing agent and of the bonds gained by all the atoms of the reducing agent, we will apply it:



The oxidizing agent is the oxygen of one molecule of  $\text{H}_2\text{O}_2$  and the reducing agent is the oxygen of another molecule of  $\text{H}_2\text{O}_2$ . The two oxygen atoms in one molecule of  $\text{H}_2\text{O}_2$  possess *together* a number of bonds the algebraic sum of which is clearly  $-2$ . Each oxygen atom of the  $\text{H}_2\text{O}_2$ , then, has a polarity-value represented by  $-1$ . In one of the products this value has changed to  $-2$ , and in the other to 0. The two oxygen atoms of one molecule of the oxidizing agent accordingly lost 2 units of polarity-value in forming water, and the two oxygen atoms of one molecule of the reducing agent gained 2 units when they were set free.

Lest you should still doubt the possibility of the oxygen of  $\text{H}_2\text{O}_2$  acting as a reducing agent (we are all in the habit of calling it "a powerful oxidizing agent" because, indirectly, it *is* one in

most cases; but in its relation to still more powerful oxidizing agents the O of the  $\text{H}_2\text{O}_2$  is a reducing agent, for the terms "oxidizing agent" and "reducing" agent are only relative terms), we will now see what happens when  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  meet in the presence of an acid:



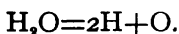
The algebraic sum of the bonds of the O in the  $\text{H}_2\text{O}_2$  is  $-2$ ; in the free oxygen it is 0; the Mn of the  $\text{KMnO}_4$  has a polarity-value of  $+7$ , but in  $\text{MnSO}_4$  it has been reduced to  $+2$ . Hence the rule requires us to put 5 in front of the  $\text{H}_2\text{O}_2$  and 2 in front of the  $\text{KMnO}_4$ . The two manganese atoms of the  $2\text{KMnO}_4$  lost 10 bonds and the ten oxygen atoms of the  $5\text{H}_2\text{O}_2$  gained those 10 bonds. But if you prefer to hold to the generally accepted conclusion that *every two molecules of potassium permanganate, in oxidation, give up 5 atoms of oxygen*, then only 5 oxygen atoms could come from the  $5\text{H}_2\text{O}_2$  in which case you will admit that our rule will still apply and bring precisely the same final result when interpreted correctly as shown in the equation  $2\text{H}_2\text{O}_2 + 2\text{H}_2\text{O}_2 = 4\text{H}_2\text{O} + 4\text{O}$ , which, reduced to its lowest terms, gives us  $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}$ , which, in turn, multiplied by 5, gives us  $5\text{H}_2\text{O}_2 = 5\text{H}_2\text{O} + 5\text{O}$ . As a matter of fact, then, it would seem quite probable that 5 of the molecules of water and 5 of the free oxygen atoms came from the  $5\text{H}_2\text{O}_2$  and that the 3 other molecules of water were formed out of the 6 hydrogen atoms of the  $3\text{H}_2\text{SO}_4$  and 3 out of the 8 oxygen atoms of the  $2\text{KMnO}_4$  (which furnished the other 5 atoms of free oxygen); but in view of the extraordinary oxidizing power of  $\text{KMnO}_4$ , it is as reasonable to regard the  $\text{H}_2\text{O}_2$  as a reducing agent in this particular reaction as it would be to regard it as neither a reducing agent nor an oxidizing agent. In this case it is certainly *not an oxidizing agent*.

## CHAPTER XXII.

### EXAMPLES IN OXIDATION AND REDUCTION.

#### 435. *Reactions of Dissociation.*

1. The decomposition of water is represented by the equation

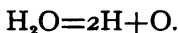


It is so simple that no rule is necessary to balance it. Nevertheless we will apply the rule in order to test it and learn its use.

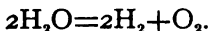
As there is but one factor, that one factor must contain both the oxidizing element and the reducing element. The H is the oxidizing agent for its polarity-value in  $\text{H}_2\text{O}$  is  $+1$ , whereas in  $2\text{H}$  it is 0. The O is the reducing agent for it has a polarity-value of  $-2$  in  $\text{H}_2\text{O}$  but of 0 in the free state. The O loses bonds but gains polarity-value.

The hydrogen loses bonds and also loses polarity-value.

As the two atoms of hydrogen in the molecule of  $\text{H}_2\text{O}$  lost 2 units of polarity-value and as the one atom of oxygen of the  $\text{H}_2\text{O}$  gained the same number of units, the equation is already balanced; but under the rule we should multiply the oxidizing agent ( $\text{H}_2\text{O}$ ) by two and the reducing agent (the same  $\text{H}_2\text{O}$ ) also by two. This would give us  $4\text{H}_2\text{O} = 8\text{H} + 4\text{O}$ , which reduced to its simplest terms is



2. Let us now write the same reaction as the foregoing with the only difference that molecular formulas are used instead of representing the uncombined elements as atoms:

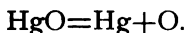


The result is clearly the same as in example 1.

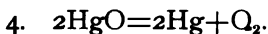
It makes no difference whether we regard a liberated element as consisting of free atoms having a polarity-value of 0, or as molecules of the same polarity-value (zero), or whether we recognize one of the atoms of the diatomic elemental molecule as having positive polarity and combining value and the other as having negative polarity and combining value. But if we treat one of

the uncombined elements as if it consisted of molecules composed of atoms of opposite polarity, then we must treat the other element in the same way. Adopting this plan we find that one of the hydrogen atoms of the  $\text{H}_2\text{O}$  did not change its polarity-value at all, while the other lost 2 bonds, for both of the hydrogen atoms in  $\text{H}_2\text{O}$  have a polarity-value of  $+1$ , whereas in  $\text{H}_2$  one of the hydrogen atoms has a polarity-value of  $+1$  and the other a polarity-value of  $-1$ . The oxygen atom in  $\text{H}_2\text{O}$  has a polarity-value of  $-2$ ; one of the oxygen atoms in the  $\text{O}_2$  has a polarity-value of  $+2$  and the other  $-2$ . The 4 bonds lost by two of the hydrogen atoms of the two molecules of water give the 4 units of polarity-value gained by one of the oxygen atoms.

3. The student should now compare the following equation with example 1:



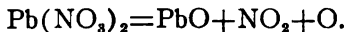
Two units were lost by the Hg and these were gained by the O.



This equation differs from example 2 in the fact that one of the elements consists of monatomic molecules. The total units transferred are 4.

5. The equation  $\text{I}_2=2\text{I}$  represents the dissociation of diatomic molecules of iodine into monatomic molecules. In the molecule  $\text{I}_2$  one of the iodine atoms has the polarity-value of  $+1$ ; the other  $-1$ . One of the atoms lost one unit; the other gained that unit. Each lost 1 bond.

6. When lead nitrate is strongly heated it splits up into  $\text{PbO}$ ,  $\text{NO}_2$ , and O. We, therefore, write the equation:



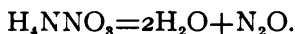
Upon examination we find that this equation is not balanced but that two molecules of  $\text{NO}_2$  are formed, so that the corrected equation is



The nitrogen in the nitrate has a polarity-value of  $+5$ ; but the nitrogen in  $\text{NO}_2$  has a polarity-value of only  $+4$ . The O in  $\text{Pb}(\text{NO}_3)_2$  and in  $\text{PbO}$  has a polarity-value of  $-2$ , but the one

oxygen atom set free has a polarity-value of 0; hence that oxygen atom gained 2 units which were transferred to it by the two nitrogen atoms in  $\text{Pb}(\text{NO}_3)_2$ .

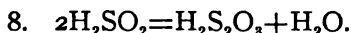
7. Ammonium nitrate when heated to complete decomposition gives water and nitrogen monoxide:



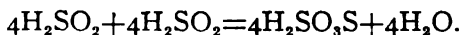
One nitrogen atom gained 4 units of polarity-value and the other lost them. Each lost 4 bonds.

The respective polarity-values of the two nitrogen atoms in the ammonium nitrate may be more readily seen when the molecular formula is written  $\text{H}_4\text{NONO}_2$ , from which it appears that the first nitrogen atom has a polarity-value of  $-3$  and the second a value of  $+5$ . In the  $\text{N}_2\text{O}$  both nitrogen atoms have the polarity-value  $+1$ . Here we have a complete equalization of polarity-values of the oxidizing and reducing atoms.

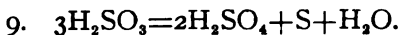
The valence (not polarity-value) of the first nitrogen atom of the  $\text{H}_4\text{NNO}_3$  is 5 and that of the other nitrogen atom is also 5. The total number of valence units (not units of polarity-value) in the  $\text{H}_4\text{NNO}_3$  is 20, namely 4 hydrogen bonds, 10 nitrogen bonds and 6 oxygen bonds; but the total number of valence units in the molecules of the products are only 12, namely 4 hydrogen bonds, 2 nitrogen bonds and 6 oxygen bonds; the difference between the totals is 8 nitrogen bonds. This difference is accounted for by the fact that eight nitrogen bonds suffered a complete reversal of polarity for 6 of the nitrogen bonds in the  $\text{H}_4\text{NNO}_3$  were positive bonds and 4 were negative, whereas 4 of the 6 positive nitrogen bonds changed to negative bonds and the 4 negative bonds changed to positive bonds thus cancelling each other, and the polarity of both of the nitrogen atoms of the  $\text{N}_2\text{O}$  is positive whereas the first nitrogen atom of the  $\text{H}_4\text{NNO}_3$  was of negative polarity.



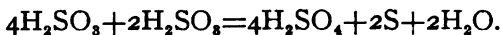
Here the S of the  $\text{H}_2\text{SO}_2$  has a polarity-value of  $+2$ , whereas the acidic sulphur atom of the  $\text{H}_2\text{SO}_3$  has a polarity-value of  $+6$  and the negative sulphur atom of that molecule has a polarity-value of  $-2$ . To illustrate the application of our rule in this case we write



The S of the first  $\text{H}_2\text{SO}_2$  gains 4 units, and that of the second  $\text{H}_2\text{SO}_2$  loses 4 units. One sulphur atom acquired 4 additional bonds; the other has 2 bonds after as well as before the reaction.



Here the S of the  $\text{H}_2\text{SO}_3$  has the polarity-value +4; the S in  $\text{H}_2\text{SO}_4$  has a value of +6; and the free S a polarity-value of 0. Hence we write:



10.  $\text{H}_2\text{SO}_3\text{S} = \text{SO}_2 + \text{S} + \text{H}_2\text{O}$  according to the rule becomes  $2\text{H}_2\text{SO}_3\text{S} + 2\text{H}_2\text{SO}_3\text{S} = 4\text{SO}_2 + 4\text{S} + 4\text{H}_2\text{O}$ , which is then reduced to its lowest terms.

#### 436. *Reactions of Synthesis.*

11. In the equation  $2\text{H} + \text{O} = \text{H}_2\text{O}$  we can see that two hydrogen atoms are required because the oxygen lost 2 units of polarity-value and that one oxygen atom is sufficient because each hydrogen atom gained 1 bond.

12. In  $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$  we find that one of the oxygen atoms of the molecule  $\text{O}_2$  lost 4 units, its polarity-value being changed from +2 to -2 while the polarity-value of the other oxygen atom is unchanged. The 4 units lost by the oxygen atom were gained by two of the hydrogen atoms of the  $2\text{H}_2$  which changed their polarity-value from -1 to +1 each of the two atoms referred to gaining 2 positive bonds, the difference between -1 and +1.

13. When monatomic molecules of iodine are condensed to diatomic molecules:



one of the iodine atoms of the  $2\text{I}$  acquires a positive bond or gains one unit of polarity-value, while the other loses one unit, becoming negative.

14. The reaction  $\text{Hg} + \text{O} = \text{HgO}$ , or  $2\text{Hg} + \text{O}_2 = 2\text{HgO}$  may be analysed and compared with examples 11 and 12.

15. In  $\text{Fe} + 2\text{I} = \text{FeI}_2$  the iron atom gains 2 units from the 2 iodine atoms.

In  $\text{Fe} + \text{I}_2 = \text{FeI}_2$  the iron atom gains 2 units from one of the iodine atoms.

16. If we assume that the molecule of iron is diatomic and on that basis write  $\text{Fe}_2 + 2\text{I}_2 = 2\text{FeI}_2$ , then only one iron atom is oxi-

dized gaining 4 units because it changes its polarity-value from  $-2$  to  $+2$ ; those four units come from those two iodine atoms which change their polarity-value each from  $+1$  to  $-1$ .

Two iron bonds have their polarity completely reversed; but the total valence units are the same in both members of the equation because two iodine bonds have their polarity reversed in the opposite direction.

17. In the equation  $\text{Fe} + 3\text{Cl} = \text{FeCl}_3$  the iron atom changes its polarity-value from 0 to  $+3$ , thus gaining 3 units; these units were furnished by the three chlorine atoms which each changed their polarity-value from 0 to  $-1$ .

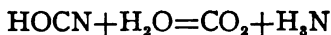
18.  $\text{FeCl}_2 + \text{Cl} = \text{FeCl}_3$  shows that the iron atom of the  $\text{FeCl}_2$  changed its polarity-value from  $+2$  to  $+3$ ; its added unit of value came from the free chlorine atom.

19. In the equation  $\text{KCN} + \text{S} = \text{KSCN}$  we are justified in assuming that the atomic linking in the molecule KCN is  $\text{K}-\text{C}\equiv\text{N}$  and that the atomic linking in KSCN is  $\text{K}-\text{S}-\text{C}\equiv\text{N}$ . Hence the polarity-value of the nitrogen atoms in both compounds must be  $-3$ ; that of the carbon in KCN is  $+2$ , and in KSCN  $+4$ ; that of the free sulphur 0, and that of the sulphur in KSCN  $-2$ .

The rule would accordingly give us  $2\text{KCN} + 2\text{S} = 2\text{KSCN}$  which we reduce by means of the common divisor 2.

Two units of polarity-value were transferred from the sulphur atom to the carbon atom.

That the molecular formulas are probably as here indicated is shown by the equation



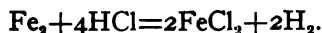
in which there is no change of polarity-value of any element.

#### 437. Substitution Reactions.

20. In the equation  $\text{Zn} + 2\text{HCl} = \text{ZnCl}_2 + 2\text{H}$  the Zn is the reducing agent, and as it gains 2 bonds it is necessary to use two molecules of the HCl the hydrogen of which is the oxidizing agent because it changes its polarity-value from  $+1$  to 0.

21. In  $\text{Fe} + 2\text{HCl} = \text{FeCl}_2 + 2\text{H}$  the conditions are precisely analogous to those noted in example 20.

If we assume that the molecule of iron is diatomic we might write:

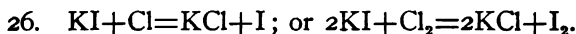
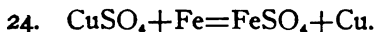


One of the iron atoms of the  $\text{Fe}_2$  is negative and the other positive. One of the hydrogen atoms of each molecule of  $\text{H}_2$  is negative and the other positive. But both of the iron atoms are positive in the  $2\text{FeCl}_2$  and all of the hydrogen atoms in the  $4\text{HCl}$  are positive. Thus one iron atom gained four units and two of the hydrogen atoms of the  $\text{HCl}$  lost them.

22. In  $\text{Fe} + \text{H}_2\text{SO}_4 = \text{FeSO}_4 + 2\text{H}$  we can see that  $\text{Fe}$  is the reducing agent gaining 2 bonds, and the  $\text{H}$  of the  $\text{H}_2\text{SO}_4$  is the oxidizing agent for its two hydrogen atoms lose two bonds. Under the rule we would, therefore, write the number 2 before each factor; but upon reducing the equation to its simplest terms we find that one molecule of each will suffice.

If we write  $\text{Fe} + \text{H}_2\text{SO}_4 = \text{FeSO}_4 + \text{H}_2$  then the two units gained by the  $\text{Fe}$  are both lost by the *one* hydrogen atom which acquired a polarity-value of  $-1$  in the molecule  $\text{H}_2$ .

23. In  $\text{FeCl}_2 + \text{Zn} = \text{ZnCl}_2 + \text{Fe}$ , the number of bonds transferred is 2.



**438.** *Reduction by hydrogen or by carbon.*

27. In the equation  $\text{Fe}_2\text{O}_3 + 6\text{H} = 2\text{Fe} + 3\text{H}_2\text{O}$  it will be seen that the iron atoms lose 6 bonds, which requires that 6 atoms of hydrogen be taken, and as each hydrogen atom gains 1 bond only one molecule of  $\text{Fe}_2\text{O}_3$  is required.

28. The equation  $\text{SO}_2 + 6\text{H} = \text{H}_2\text{S} + 2\text{H}_2\text{O}$  shows that the  $\text{S}$  is reduced from a polarity-value of  $+4$  to one of  $-2$ , which is a loss of 6 units.

29. In  $\text{KIO}_3 + 3\text{C} = \text{KI} + 3\text{CO}$  the reason for the number 3 before the  $\text{C}$  is that the application of the rule requires 6 atoms of carbon and 2 molecules of  $\text{KIO}_3$ , for the  $\text{I}$  of the  $\text{KIO}_3$ , being reduced from  $+5$  to  $-1$ , loses 6 units, while each carbon atom gains 2 units of polarity-value; but we reduce  $2\text{KIO}_3 + 6\text{C} = 2\text{KI} + 6\text{CO}$  to its simplest terms by dividing all the co-efficients placed before the factors and products by the common divisor 2.

30. In the equation  $\text{CaSO}_4 + 3\text{C} = \text{CaS} + 2\text{CO} + \text{CO}_2$  we find that the  $\text{S}$  is reduced from a polarity-value  $+6$  to one of  $-2$ , thus losing 8 units. We further find that the  $\text{C}$  is oxidized from

a value of 0 to +2 in one of the products and to +4 in another product. This proves to be, then, a case of *double oxidation and reduction*.

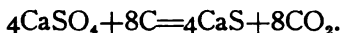
There are *two* separate transfers of polarity-value, but the oxidizing agent and reducing agent are the same in both. The rule, however, applies as follows: Having written the factors and products



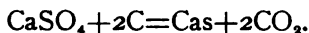
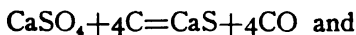
we find that one of the transfers of polarity-value is that by which the carbon forms CO and that this requires us to put the number 2 before the CaSO<sub>4</sub> and the number 8 before the C, resulting in the equation



while the second transfer calls for the equation



These equations, reduced to their simplest terms, will be



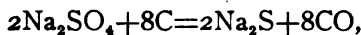
Adding these together we get



and this, reduced to its simplest terms, brings the final result:



31.  $\text{Na}_2\text{SO}_4 + 4\text{C} = \text{Na}_2\text{S} + 4\text{CO}$ . This equation is deduced from



for S loses 8 units of polarity-value and the C gains 2 units; hence the units lost from the  $2\text{Na}_2\text{SO}_4$  must be  $2 \times 8 = 16$ , and those gained by the C must be  $8 \times 2 = 16$ .

32. When sulphuric acid is heated with carbon the products are water, sulphur dioxide and carbon dioxide. Hence we write:



Upon examination we find that this equation does not balance, for we have only four oxygen atoms in the first member of the equation and five in the other. To balance it we apply the rule

as follows: As the S is reduced from +6 to +4, thus losing 2 units of polarity-value, we put the number 2 before the C, and as the C gains four positive bonds, changing its polarity-value from 0 to +4, we put 4 before the oxidizing agent, which gives us



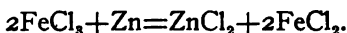
which we reduce to



33. In the equation  $\text{H}_2\text{SO}_3 + 2\text{H} = \text{H}_2\text{SO}_2 + \text{H}_2\text{O}$  the sulphur gives up 2 positive bonds to the hydrogen.

439. *Reduction by metals.*

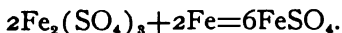
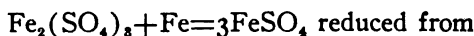
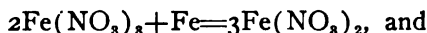
34. Zinc reduces ferric chloride to ferrous chloride as represented by



As the iron atom in one molecule of  $\text{FeCl}_3$  loses 1 bond we require only one atom of Zn, and as the Zn gains 2 bonds we take 2 molecules of the  $\text{FeCl}_3$ .

35. In the equation  $2\text{FeCl}_3 + \text{Fe} = 3\text{FeCl}_2$  we find that the iron of the  $\text{FeCl}_3$  is the oxidizing agent and the uncombined Fe is the reducing agent.

36. The following equations may be understood by comparison with the foregoing:



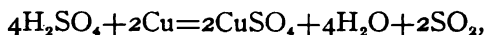
37. In the equation  $2\text{HgCl}_2 + \text{Fe} = 2\text{HgCl} + \text{FeCl}_2$  it is seen that the mercury is reduced from +2 to +1 and the iron oxidized from 0 to +2.

38. When copper is heated with sulphuric acid the products are cupric sulphate, water and sulphur dioxide, so we write  $\text{H}_2\text{SO}_4 + \text{Cu} = \text{CuSO}_4 + \text{H}_2\text{O} + \text{SO}_2$ .

To balance this equation we put 2 before the  $\text{H}_2\text{SO}_4$  because the Cu gains 2 bonds, and we need also two atoms of copper since the S of the  $\text{H}_2\text{SO}_4$  loses 2 bonds. This would give us



which we see can not be balanced. This is because the rule applied does not always provide all of the factors necessary to *complete the whole equation*, although it does always lead to correct proportions of the oxidizing agent and reducing agent necessary to effect the oxidation and reduction or transfer of polarity-value. This equation may be easily completed, however, for we know that the 2 molecules of sulphuric acid called for by the rule must be *consumed* for the oxidation and hence can not do more than to furnish the units of polarity-value required by the Cu, and as two atoms of Cu must form two molecules of  $\text{CuSO}_4$ , each requiring an additional molecule of sulphuric acid to furnish the sulphate radical,  $\text{SO}_4$ , we finally get



which we reduce to



39. In the reaction  $\text{Hg}(\text{NO}_3)_2 + \text{Hg} = 2\text{HgNO}_3$  it is seen that the mercury atom of the  $\text{Hg}(\text{NO}_3)_2$  gives up one bond to the uncombined mercury.

40. The production of mercuric oxide by heating a mixture of mercuric nitrate and mercury is sometimes represented by the equation  $\text{Hg}(\text{NO}_3)_2 + \text{Hg} = 2\text{HgO} + 2\text{NO}_2$ .

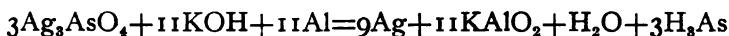
Here the nitrogen atoms of the mercuric nitrate lose together 2 bonds, which are taken up by the uncombined mercury as it takes part in forming the  $\text{HgO}$ . The application of the rule gives  $2\text{Hg}(\text{NO}_3)_2 + 2\text{Hg} = 4\text{HgO} + 4\text{NO}_2$ , which can be reduced as shown.

41. In the equation  $3\text{NaHSO}_3 + \text{Zn} = \text{NaHSO}_2 + \text{Na}_2\text{SO}_3 + \text{ZnSO}_3 + \text{H}_2\text{O}$  we can readily see that there is but one transfer of polarity-value, the S of one molecule of  $\text{NaHSO}_3$  losing 2 bonds for it has a polarity-value of +4 in the  $\text{NaHSO}_3$ , but of only +2 in the  $\text{NaHSO}_2$ , and the 2 bonds lost by the S are taken up by the Zn. The rule would, therefore, require, *for the oxidation and reduction*, 2 molecules of  $\text{NaHSO}_3$  and 2 atoms of Zn. But as we know the products to be not only  $\text{NaHSO}_2$ , but also  $\text{ZnSO}_3$  and  $\text{Na}_2\text{SO}_3$ , it is evident that 4 additional molecules of the  $\text{NaHSO}_3$  are required for the formation of these salts, so that we would then have  $6\text{NaHSO}_3 + 2\text{Zn} = 2\text{NaHSO}_2 + 2\text{Na}_2\text{SO}_3 + 2\text{ZnSO}_3 + 2\text{H}_2\text{O}$ , which we can divide by the common divisor 2 to reduce the equation to its lowest terms.

42. The equation  $\text{Pb}(\text{NO}_3)_2 + 6\text{KOH} + 6\text{Al} = \text{Pb} + 6\text{KAlO}_2 + 2\text{H}_3\text{N}$  discloses the fact that the oxidizing agents are contained in the  $\text{Pb}(\text{NO}_3)_2$ , which in this case contains one atom of one element and two atoms of another element, which together give up 18 units of polarity-value for the Pb loses 2 units and each nitrogen atom 8. Each atom of Al, which is the reducing agent, gains 3 bonds. But instead of writing  $3\text{Pb}(\text{NO}_3)_2 + 18\text{KOH} + 18\text{Al} = 3\text{Pb} + 18\text{KAlO}_2 + 6\text{H}_3\text{N}$ , which the application of the rule would give, we reduce that equation to its lowest terms by means of the common divisor 3.

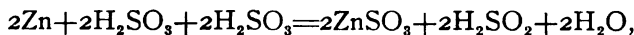
43. Setting down the known factors and products of the following reaction,  $\text{Ag}_3\text{AsO}_4 + \text{KOH} + \text{Al} = \text{Ag} + \text{KAlO}_2 + \text{H}_2\text{O} + \text{H}_3\text{As}$ , we then proceed to balance the equation as follows:

We find that the  $\text{Ag}_3\text{AsO}_4$  contains the oxidizing agents, and that each molecule of it furnishes 11 units of polarity-value for the three silver atoms give up 1 unit each and the As gives up 8 units, the As being reduced from a polarity-value of +5 to one of -3 which we find it has in the  $\text{H}_3\text{As}$ . The Al is the reducing agent for it gains 3 bonds, changing its polarity-value from 0 to +3. Under the rule, therefore, we should find that 3 molecules are required of the factor containing the oxidizing agents and 11 atoms of the elemental reducing agent, and these proportions give the equation



for 11 molecules are required of the KOH to form the 11KAlO<sub>2</sub>.

44. In the following equation the zinc gains 2 bonds, which it takes from the sulphur of one-half of the molecules of  $\text{H}_2\text{SO}_3$ .



which we reduce to  $\text{Zn} + 2\text{H}_2\text{SO}_3 = \text{ZnSO}_3 + \text{H}_2\text{SO}_2 + \text{H}_2\text{O}$ .

One-half of the  $\text{H}_2\text{SO}_3$  goes to form the  $\text{ZnSO}_3$ .

## CHAPTER XXIII.

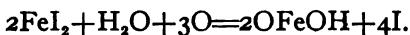
### EXAMPLES OF OXIDATION REACTIONS—CONTINUED.

#### 440. *Oxidation by oxygen.*

45. In the equation  $\text{CS}_2 + 6\text{O} = \text{CO}_2 + 2\text{SO}_2$  it will be seen that the two sulphur atoms of the molecule  $\text{CS}_2$  each gained 6 units of polarity-value, for the polarity-value of each was increased from  $-2$  to  $+4$ . The oxygen furnished these units. The rule would give us:  $2\text{CS}_2 + 12\text{O} = 2\text{CO}_2 + 4\text{SO}_2$ .

46. When a solution of ferrous iodide is exposed to the air the iodide is decomposed, iodine is liberated and a precipitate of  $\text{OFeOH}$  is formed. The factors are ferrous iodide, water and oxygen. Hence we write  $\text{FeI}_2 + \text{H}_2\text{O} + \text{O} = \text{OFeOH} + \text{I}$ .

To balance this equation we first identify the oxidizing and reducing agents. We find that the  $\text{FeI}_2$  contains the reducing agents and  $\text{O}$  the oxidizing agent. The atoms composing one molecule of  $\text{FeI}_2$  gain together 3 units for the iron gains 1 and each iodine atom 1; hence we require 3 atoms of the oxygen. The oxygen loses 2 units; hence we require 2 molecules of the  $\text{FeI}_2$ . Our equation consequently becomes



47. The equation  $2\text{SO}_2 + 2\text{O} + \text{N}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{HOSO}_2\text{ONO}$  shows that the S of the  $\text{SO}_2$  is the reducing agent and the O the oxidizing agent, for the S changes its polarity-value from  $+4$  to  $+6$ , while the O changes its value from 0 to  $-2$ . The O gains bonds but loses polarity-value.

When water reacts with the compound  $\text{HOSO}_2\text{ONO}$  the polarity-value of the S in that compound is at once disclosed, for the equation is  $2\text{HOSO}_2\text{ONO} + \text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 + \text{N}_2\text{O}_5$ , in which reaction there is no change of polarity-value of any element.

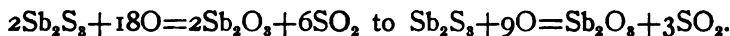
48. When antimonous sulphide,  $\text{Sb}_2\text{S}_3$ , is roasted in the air it produces antimonous oxide and sulphur dioxide. We write



To balance this equation we identify the S of the  $\text{Sb}_2\text{S}_3$  as

the reducing agent for it changes its polarity-value from  $-2$  to  $+4$ , a difference or increase of 6 units for each sulphur atom or 18 units for the three atoms. The oxygen changes its polarity-value from 0 to  $-2$ . Under the rule we accordingly put the number 18 in front of the O and the number 2 in front of the  $\text{Sb}_2\text{S}_3$ , which makes the total units transferred 36.

But we can reduce

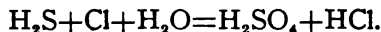


If we transpose this equation to  $2\text{Sb}_2\text{S}_3 + 9\text{O}_2 = 2\text{Sb}_2\text{O}_3 + 6\text{SO}_2$  we shall find that the two factors contain 24 tied positive bonds and 24 negative bonds; but the products contain 30 tied positive bonds and 30 negative bonds. The difference is accounted for by the fact that the six sulphur bonds of the  $2\text{Sb}_2\text{S}_3$  suffered a complete reversal of polarity.

**441.** *The halogens as oxidizing and reducing agents.*

49. The equation  $\text{FeCl}_2 + \text{Cl} = \text{Fe}_2\text{Cl}_3$  is easily seen to balance, and the transfer of one unit of polarity-value from the Cl to the Fe is apparent.

50. Chlorine oxidizes  $\text{H}_2\text{S}$  to  $\text{H}_2\text{SO}_4$  in the presence of water, the chlorine forming HCl. We write



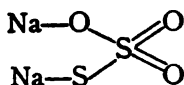
To make this equation balance we write 8 before the Cl because the S of the  $\text{H}_2\text{S}$  gained 8 units in changing its polarity-value from  $-2$  to  $+6$ . The chlorine changes its polarity-value from 0 to  $-1$ , so that one molecule of  $\text{H}_2\text{S}$  suffices. But as all of the chlorine taken must form 8HCl we must add to the factors ( $\text{H}_2\text{S}$  and 8Cl) four molecules of  $\text{H}_2\text{O}$ .

51. In the equation  $\text{K}_4\text{Fe}(\text{CN})_6 + \text{Cl} = \text{K}_3\text{Fe}(\text{CN})_6 + \text{KCl}$  we find that the iron gained 1 unit of polarity-value which the chlorine lost.

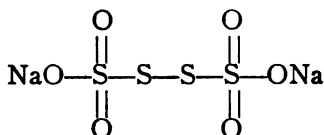
52. In the equation  $\text{NaHSO}_3 + 2\text{I} + \text{H}_2\text{O} = \text{NaHSO}_4 + 2\text{HI}$  it is easily discovered that the S gained 2 units of polarity-value at the expense of the iodine.

53. In  $\text{Na}_2\text{SO}_3 + \text{Na}_2\text{S} + 2\text{I} = \text{Na}_2\text{SO}_3\text{S} + 2\text{NaI}$  we see that the acidic sulphur of the  $\text{Na}_2\text{SO}_3$ , which has a polarity-value of  $+4$ , reappears as the acidic sulphur of the  $\text{Na}_2\text{SO}_3\text{S}$  with a polarity-value of  $+6$ ; it, therefore, gained 2 bonds. Hence we need 2 atoms of the I, which is the oxidizing agent.

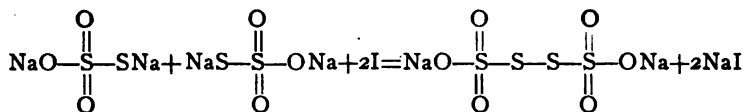
54. In  $2\text{Na}_2\text{SO}_3\text{S} + 2\text{I} = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$  we can not readily discover the disposition of the 2 units of polarity-value given up by the two iodine atoms. That one of the sulphur atoms in the  $\text{Na}_2\text{SO}_3\text{S}$  has a polarity-value of +6 and the other a polarity-value of -2 we have assumed in example 48. If we now assume, further, that the structure of the sodium thiosulphate is



and that the sodium tetrathionate,  $\text{Na}_2\text{S}_4\text{O}_6$  is

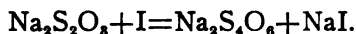


we shall be able to represent the reaction as follows:



and it is evident that of the two middle atoms of sulphur in the tetrathionate one must have a valence of 0 and the other a valence of -2, for no two atoms can be connected with each other except by bonds of opposite polarity. Both of these sulphur atoms had a polarity-value of -2 in the  $\text{Na}_2\text{SO}_3\text{S}$ ; hence one of them gained the 2 units of polarity-value given up by the iodine.

We may, however, proceed as follows:



Here we find that if the two bonds of the sodium atoms be deducted from the six bonds of the oxygen atoms of the  $\text{Na}_2\text{S}_2\text{O}_3$ , we shall have a remainder of 4 bonds, which indicates that the algebraic sum of the units of polarity-value of the two sulphur atoms must be +4. In the same manner we find that the algebraic sum of the units of polarity-value of the four sulphur atoms in  $\text{Na}_2\text{S}_4\text{O}_6$  must be +10 (see paragraph 195), one-

half of which (for 2 atoms of sulphur) is +5. Hence the two sulphur atoms of one molecule of  $\text{Na}_2\text{S}_2\text{O}_8$ , when entering into the formation of  $\text{Na}_2\text{S}_4\text{O}_6$ , must together gain 1 unit of polarity-value, which is given up by one atom of iodine. One molecule of the  $\text{Na}_2\text{S}_2\text{O}_8$  and one atom of I are therefore the *proportions* required by the rule *to account for the oxidation and reduction* or transfer of polarity-value. But the formation of  $\text{Na}_2\text{S}_4\text{O}_6$  calls for 2 molecules of  $\text{Na}_2\text{S}_2\text{O}_8$ , so that both factors must be doubled, whence we get  $2\text{Na}_2\text{S}_2\text{O}_8 + 2\text{I} = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$ .

When  $\text{H}_2\text{S}_4\text{O}_6$  breaks down into sulphuric acid, sulphur dioxide and sulphur, as represented by the equation  $\text{H}_2\text{S}_4\text{O}_6 = \text{H}_2\text{SO}_4 + \text{SO}_2 + 2\text{S}$ , we find that one of the two sulphur atoms which in the  $\text{H}_2\text{S}_4\text{O}_6$  had each a polarity-value of +6 retains that polarity-value in the  $\text{H}_2\text{SO}_4$ , while the other lost 2 units in forming  $\text{SO}_2$ ; the 2 units lost by that sulphur atom were taken up by the sulphur atom which in the  $\text{Na}_2\text{S}_4\text{O}_6$  had a polarity-value of -2.

55. The equation  $(\text{H}_4\text{N})_2\text{S} + 2\text{I} = 2\text{H}_4\text{NI} + \text{S}$  will be easily understood.

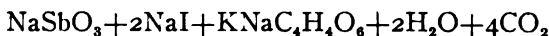
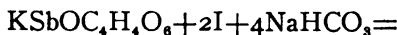
56. In  $\text{KPH}_2\text{O}_2 + 4\text{I} + 2\text{H}_2\text{O} = \text{KI} + \text{H}_3\text{PO}_4 + 3\text{HI}$  we find that the polarity-value of the P in the  $\text{KPH}_2\text{O}_2$  is +1, while that of the P in  $\text{H}_3\text{PO}_4$  is +5; the difference is 4, which, under the rule, calls for 4 atoms of the iodine. Each iodine atom lost 1 unit of polarity-value, so that one molecule of  $\text{KPH}_2\text{O}_2$  must be taken.

57. In the equation



the two atoms of arsenic gain together 4 units of polarity-value which are taken up from the 4I.

58. In the equation



we see that the Sb in the "tartar emetic" has a polarity-value of +3, and in the sodium antimonite its value is +5; it acquired 2 additional units of polarity-value from the 2I.

59.  $\text{H}_2\text{SO}_3 + \text{H}_2\text{O} + 2\text{I} = \text{H}_2\text{SO}_4 + 2\text{HI}$  shows that the S gained

2 units of true combining value, which were furnished by the iodine atoms.

60. In the equation  $6\text{KOH} + 6\text{I} = 5\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O}$  it will be seen that one iodine atom gained 5 units of polarity-value, which were given up by the other 5 iodine atoms.

61. In  $6\text{Ca}(\text{OH})_2 + \text{I}_2\text{Cl} = 5\text{CaCl}_2 + \text{Ca}(\text{ClO}_3)_2 + 6\text{H}_2\text{O}$  ten chlorine atoms suffer reduction from 0 to  $-1$ , and the 10 units lost by these chlorine atoms are taken up by the other two chlorine atoms which acquire a polarity-value of  $+5$ .

62. In the equation  $2\text{S}_2\text{Cl}_2 + 2\text{H}_2\text{O} = 4\text{HCl} + \text{SO}_2 + 3\text{S}$  it would seem as if the sulphur of the  $\text{S}_2\text{Cl}_2$  had a polarity-value of  $+1$ ; but the polarity-value of one atom is 0 and that of the other  $+2$ , for the structure is  $\text{Cl}-\text{S}-\text{S}-\text{Cl}$ , or  $\text{Cl}-\text{S}-\text{S}-\text{Cl}$ . One of the sulphur atoms of each molecule of  $\text{S}_2\text{Cl}_2$  neither gains nor loses combining value in being liberated; but the other two sulphur atoms of the two molecules of  $\text{S}_2\text{Cl}_2$  undergo a change of polarity-value, one of them giving its 2 units to the other, for the S in  $\text{SO}_2$  has a polarity-value of  $+4$ .

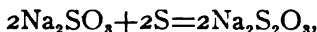
**442.** *Sulphur and phosphorus as oxidizing and reducing agents.*

63. The production of sodium thiosulphate by boiling sulphur with sodium sulphate in water is usually represented by the equation  $\text{Na}_2\text{SO}_3 + \text{S} = \text{Na}_2\text{S}_2\text{O}_3$ .

It is evident that the polarity-value of the S in the  $\text{Na}_2\text{SO}_3$  is  $+4$ , and that the polarity-value of the uncombined S is 0.

But what is the polarity-value of each sulphur atom in the  $\text{Na}_2\text{S}_2\text{O}_3$ ?

If we deduct the two sodium bonds from the six oxygen bonds of the molecule  $\text{Na}_2\text{S}_2\text{O}_3$  the remainder is four. From this we could conclude that each sulphur atom in that molecule has a polarity-value of  $+2$ . Assuming that this is correct we would conclude that the S of the  $\text{Na}_2\text{SO}_3$  lost 2 units in forming the  $\text{Na}_2\text{S}_2\text{O}_3$  and that the free S gained 2 units. Applying the rule on that principle would give us the correct equation,



which we can reduce to its lowest terms by means of the common divisor 2.

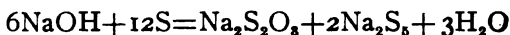
But as a matter of fact the polarity-value of the S in  $\text{Na}_2\text{S}_2\text{O}_3$  is not  $+2$ , for the structure of the molecule is as shown in ex. 54,

so that the molecular formula should be written  $\text{Na}_2\text{SO}_3\text{S}$ . From this it is apparent that one of the sulphur atoms has a polarity-value of  $+6$  and the other a polarity-value of  $-2$ .

The sulphur of the  $\text{Na}_2\text{SO}_3$  reappears in the  $\text{Na}_2\text{SO}_3\text{S}$  with a polarity-value of  $+6$ ; but the free sulphur used as a factor is that which reappears in the product with a polarity-value of  $-2$ . The application of the rule on this basis gives the same result as before.

64. In the equation  $\text{Sb}_2\text{S}_3 + 3\text{Na}_2\text{S} + 2\text{S} = 2\text{Na}_3\text{SbS}_4$  we identify the antimony of the  $\text{Sb}_2\text{S}_3$  as the element which is oxidized and the free sulphur as the oxidizing agent. The rule would give us  $2\text{Sb}_2\text{S}_3 + 6\text{Na}_2\text{S} + 4\text{S} = 4\text{Na}_3\text{SbS}_4$ .

65. In the equation



we find that we have free sulphur with a polarity-value of 0 as one of the factors. What its polarity-value is in the products we will now try to discover.

That sodium can assume a polarity-value of  $+5$ , which it must have in the molecule  $\text{Na}_2\text{S}_5$  if the sulphur atoms are all directly united to the sodium, would be a violent assumption. It is reasonable to take for granted that the sodium in that compound has its usual polarity-value of  $+1$ . On that basis the structure of the so-called "sodium pentasulphide," assuming that it is really a *sulphide*, must be  $\text{Na}-\text{S}-\text{S}-\text{S}-\text{S}-\text{S}-\text{Na}$ , in which one sulphur atom has a polarity-value of  $-2$ , while the polarity-value of all the other four sulphur atoms would then be 0. We may accordingly write:  $\text{NaOH} + \text{S} + \text{S} = \text{Na}_2\text{S}_2\text{O}_3 + \text{Na}_2\text{S}_4\text{S} + \text{H}_2\text{O}$ .

The rule is then applied as follows: As the free sulphur has a polarity-value of 0 but acquires a value of  $+2$  in the  $\text{Na}_2\text{S}_2\text{O}_3$  and of  $-2$  in  $\text{Na}_2\text{S}_4\text{S}$  we put the number 2 before the oxidizing agent S and also before the reducing agent S, which would give us  $\text{NaOH} + 2\text{S} + 2\text{S} = \text{Na}_2\text{S}_2\text{O}_3 + \text{Na}_2\text{S}_4\text{S} + \text{H}_2\text{O}$ . We know that the sulphur acting as a reducing agent formed the  $\text{Na}_2\text{S}_2\text{O}_3$  and that the sulphur acting as an oxidizing agent must form the  $\text{Na}_2\text{S}_4\text{S}$ . As we have 2 atoms of oxidizing sulphur we must get two molecules of  $\text{Na}_2\text{S}_4\text{S}$  for each molecule is assumed to contain but one sulphur atom having the polarity-value of  $-2$ . Therefore we now have  $\text{NaOH} + 2\text{S} + 2\text{S} = \text{Na}_2\text{S}_2\text{O}_3 + 2\text{Na}_2\text{S}_4\text{S} +$

$\text{H}_2\text{O}$ . To balance this equation we finally add 8 additional sulphur atoms, which enter into the two molecules of  $\text{Na}_2\text{S}_4\text{S}$  without oxidation or reduction, and we find that 6 molecules of  $\text{NaOH}$  are required, so that the final equation stands:



But  $\text{Na}_2\text{S}_2\text{O}_3$  is probably  $\text{Na}_2\text{SO}_3\text{S}$  having one acidic sulphur atom with a polarity-value of  $+6$  and a negative sulphur atom with the polarity-value  $-2$ ; and the  $\text{Na}_2\text{S}_4\text{S}$  is probably sodium tetrathiosulphate which contains one acidic sulphur atom having the polarity-value  $+6$  and four negative sulphur atoms, each with the polarity-value  $-2$ . Upon this assumption we write:



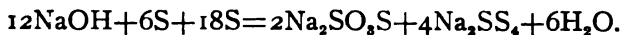
The oxidizing sulphur of the first member of the equation reappears in both products with the polarity-value  $-2$ , while the reducing agent  $\text{S}$  reappears in both products with the polarity-value  $+6$ . Hence we get



It is at once apparent that 4 molecules of  $\text{NaOH}$  must be taken to form one molecule of each of the compounds  $\text{Na}_2\text{SO}_3\text{S}$  and  $\text{Na}_2\text{SS}_4$ . Hence we get



But as the  $\text{Na}_2\text{SO}_3\text{S}$  contains three oxygen atoms it is evident that the co-efficients of all the factors must be multiples of 3. If we multiply the factors by 3 we shall get



This we can reduce to



The three sulphur atoms oxidized gained 18 units of polarity-value and the 9 sulphur atoms reduced lost those 18 units. Three molecules of the salts must be formed by the three sulphur atoms oxidized because each molecule contains one atom of acidic sulphur. But it can not be that two molecules of the  $\text{Na}_2\text{SO}_3\text{S}$  and

one molecule of  $\text{Na}_2\text{SS}_4$  are formed because we would then have only 9 sulphur atoms in three molecules of salt. If we take two molecules of  $\text{Na}_2\text{SS}_4$  and one of the  $\text{Na}_2\text{SO}_3\text{S}$  we shall then have accounted for all of the sulphur, so that this must be correct. Moreover, we know that all of the hydrogen of the  $6\text{NaOH}$  must form 3 molecules of water, leaving only 3 oxygen atoms for the formation of the  $\text{Na}_2\text{SO}_3\text{S}$ .

The most convenient method, however, for balancing this equation is that suggested in paragraph 432, as follows:



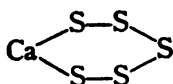
It is evident that the algebraic sum of the units of polarity-value of the sulphur in  $\text{Na}_2\text{S}_2\text{O}_3$  must be  $+4$  because the algebraic sum of the units of polarity-value of the positive sodium and the negative oxygen is  $-4$ . The algebraic sum of the units of polarity-value of the sulphur in  $\text{Na}_2\text{S}_5$  (whether it be written  $\text{Na}_2\text{SS}_4$  or in any other manner) must be  $-2$  because the algebraic sum of the units of polarity-value of the sodium is  $+2$ . Now, as the sulphur is the only element which undergoes any change of polarity-value, and as it must accordingly serve both as an oxidizing agent and a reducing agent, and must reappear in the two products, in one product with an algebraic sum of the units of polarity-value which is expressed by a minus quantity, and, in the other product, with an algebraic sum of the units of polarity-value which is a plus quantity, these sums added together must make the sum of 0 since the total units gained by the sulphur in one product must be the number lost by the sulphur in the other product. Hence, as the algebraic sum of the units of polarity-value of the sulphur in each molecule of  $\text{Na}_2\text{S}_2\text{O}_3$  is  $+4$ , and the algebraic sum of the units of polarity-value of the sulphur in each molecule of  $\text{Na}_2\text{S}_5$  is  $-2$ , we know at once that two molecules of  $\text{Na}_2\text{S}_5$  must be formed for each molecule of  $\text{Na}_2\text{S}_2\text{O}_3$ . The total number of sulphur atoms contained in one molecule of  $\text{Na}_2\text{S}_2\text{O}_3$  and two molecules of  $\text{Na}_2\text{S}_5$  is 12, and we accordingly balance the equation on that basis.

66. Calcium thiosulphate and so-called "calcium pentasulphide" are formed when calcium hydroxide and sulphur are boiled together in water, just as sodium thiosulphate and so-called sodium pentasulphide are formed when sodium hydroxide and sulphur are boiled together with water (See example 65).

This equation is usually given to represent the reaction referred to:

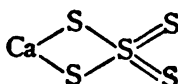


The only conceivable structure of calcium pentasulphide must be



in which it is evident that four sulphur atoms in the molecule have a polarity-value of 0 and the fifth sulphur atom a polarity-value of  $-2$ , just as in the hypothetical "sodium pentasulphide" mentioned in the preceding example.

$\text{CaS}_2\text{O}_3$  is probably  $\text{CaSO}_3\text{S}$ , and  $\text{CaS}_5$  is probably calcium tetrathiosulphate



But the easiest way to balance this equation is as follows (par. 432):

The algebraic sum of the units of polarity-value of the sulphur atoms in one molecule of  $\text{CaS}_2\text{O}_3$  is  $+4$ ; that of the sulphur atoms in one molecule of  $\text{CaS}_5$  is clearly  $-2$ . Hence we know that the products must be one molecule of  $\text{CaS}_2\text{O}_3$  and two molecules of  $\text{CaS}_5$ , all together requiring 12 atoms of sulphur.

67. In the equation



it is seen that one sulphur atom gains 6 units of polarity-value and that the other three sulphur atoms lose them.

We know that the products are one molecule of  $\text{CaS}_2\text{O}_3$  and two molecules of  $\text{CaS}$  because the sulphur atoms of  $\text{CaS}_2\text{O}_3$  have together a polarity-value of  $+4$  and those of two molecules of  $\text{CaS}$  together a polarity-value of  $-4$ . (See also Ex. 69.)

68. In  $\text{CaSO}_3\text{S} + 2\text{CaSS}_4 + 6\text{HCl} = 3\text{CaCl}_2 + 12\text{S} + 3\text{H}_2\text{O}$  we find that the only element which changes polarity-value is the

sulphur, and as all of that sulphur has a polarity-value of 0 in the products, it must be that the polarity-value of the sulphur atoms in one of the factors added to the polarity-value of the sulphur atoms in the other factor must be 0, and that two molecules of  $\text{CaSS}_4$  must, therefore, be required.

The three acidic sulphur atoms (one in the  $\text{CaSO}_3\text{S}$  and one in each molecule of the  $\text{CaSS}_4$ ) lose 18 units which are gained by the 9 negative sulphur atoms of the two salts.

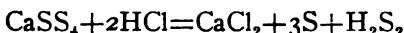
69. In  $\text{CaSO}_3\text{S} + 2\text{CaS} + 6\text{HCl} = 3\text{CaCl}_2 + 4\text{S} + 3\text{H}_2\text{O}$  we find that the acidic sulphur in  $\text{CaSO}_3\text{S}$  loses 6 units and the other three sulphur atoms gain those 6 units (See also Ex. 67).

70. In  $\text{CaSS}_4 + 2\text{HCl} = \text{CaCl}_2 + 4\text{S} + \text{H}_2\text{S}$  we see that the acidic sulphur atom of the  $\text{CaSS}_4$  loses 6 units which are taken up by three of the negative sulphur atoms while the fourth negative sulphur atom forms the  $\text{H}_2\text{S}$ .

We can see also that the algebraic sum of the units of polarity-value of the sulphur atoms of the  $\text{CaSS}_4$  ( $-2$ ) is the same as that of the sulphur atoms of the products (which is the sum of 0 and  $-2$ ).

In the equation  $\text{CaS} + 2\text{HCl} = \text{CaCl}_2 + \text{H}_2\text{S}$  there is no oxidation and reduction.

Under certain conditions we may get the reaction



and the student may not at once recognize the fact that here, too, the algebraic sum of the units of polarity-value of the sulphur atoms in each member of the equation is the same as in the other, but as  $\text{H}_2\text{S}_2$  is  $\text{H}-\text{S}-\text{S}-\text{H}$  it will be seen that one of the sulphur atoms in that molecule has a polarity-value of 0 so that the algebraic sum of the positive and negative units of polarity-value of the sulphur is the same in  $\text{H}_2\text{S} + 4\text{S}$  as in  $\text{H}_2\text{S}_2 + 3\text{S}$  or in  $\text{H}_2\text{S}_3 + 2\text{S}$  or in  $\text{H}_2\text{S}_5$ .

$\text{H}_2\text{S}_3$  is probably the sulphur acid  $\text{H}_2\text{SS}_2$  corresponding to the oxygen acid  $\text{H}_2\text{SO}_3$ , and  $\text{H}_2\text{S}_5$  is the sulphur acid  $\text{H}_2\text{SS}_4$  corresponding to  $\text{H}_2\text{SO}_4$ .

71. The equation  $3\text{K}_2\text{CO}_3 + 8\text{S} = 2\text{K}_2\text{S}_3 + \text{K}_2\text{S}_2\text{O}_3 + 3\text{CO}_2$  shows a transfer of units of polarity-value which may be accounted for as follows:

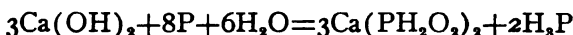
As the algebraic sum of the positive and negative bonds of the sulphur in one molecule of  $\text{K}_2\text{S}_3$  must be  $-2$  since the potassium

atoms present together 2 positive bonds, and as the algebraic sum of the units of polarity-value of the sulphur atoms in  $K_2S_2O_3$  must be +4, it follows that two molecules of  $K_2S_3$  are required to offset one molecule of  $K_2S_2O_3$  (see par. 432).

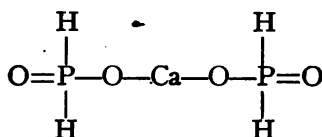
The  $K_2S_3$  is doubtless  $K_2SS_2$  or potassium hypthiosulphite (or hypodithiosulphite) corresponding to the oxygen salt  $K_2SO_3$ , while the  $K_2S_2O_3$  is  $K_2SO_3S$  or potassium thiosulphate (or monothiosulphate). [See also Ex. 72.]

72. The equation  $2K_2S_3 + K_2S_2O_3 + 6HCl = 6KCl + 8S + 3H_2O$  will be readily understood from the preceding example.

73. In the equation



we find that the phosphorus is both the oxidizing and the reducing element and it reappears in both products. In  $Ca(PH_2O_2)_2$  the two phosphorus atoms have together a polarity-value of +2 for the structure of the molecule is



That the algebraic sum of the units of polarity-value of the two phosphorus atoms together must be +2 is also evident from the fact that the calcium atom has a polarity-value of +2, the algebraic sum of the units of polarity-value of the four oxygen atoms together must be -8, and the four hydrogen atoms have 4 positive bonds. Each phosphorus atom has in reality 2 negative and 3 positive bonds and the sum of -2 and +3 is +1.

The polarity-value of the P in  $H_3P$  is clearly -3.

Now, as all of the phosphorus in  $Ca(PH_2O_2)_2$  has the polarity-value of +2 and the P in  $H_3P$  a polarity-value of -3 it is evident that three molecules of  $Ca(PH_2O_2)_2$  must be formed for every two molecules of  $H_3P$ , and that we accordingly require 8 atoms of phosphorus for the reaction and 3 molecules of  $Ca(OH)_2$ .

74. In the equation  $2SCl_2 + 2H_2O = SO_2 + 4HCl + S$  we find that the sulphur atom of one molecule of  $SCl_2$  gives up 2 units of polarity-value to the sulphur atom of the second molecule of  $SCl_2$ .

But in  $\text{OSCl}_2 + \text{H}_2\text{O} = \text{SO}_2 + 2\text{HCl}$  and in  $\text{OSCl}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_3 + 2\text{HCl}$  there is neither oxidation nor reduction for the S has the polarity-value  $+4$  in both factors and products.

In  $\text{O}_2\text{SCl}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{HCl}$  the sulphur has a polarity-value of  $+6$  in both members of the equation, so that here, also, there is no transfer of bonds.

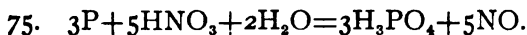
## CHAPTER XXIV.

### EXAMPLES OF OXIDATION EQUATIONS—CONTINUED.

#### 443. *Oxidation by nitric acid and other nitrates.*

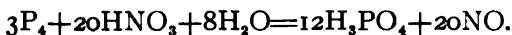
As nitric acid and other nitrates are very frequently employed as oxidizing agents a large number of examples of reactions in which nitric acid is a factor are here given. The nitrogen in nitric acid has a polarity-value of +5 as may be at once seen from its molecular formula  $\text{HNO}_3$ , for all of the negative bonds in the molecule are the six oxygen bonds one of which is canceled by the bond from the hydrogen atom leaving the other 5 negative bonds to be canceled by the 5 positive nitrogen bonds.

When nitric acid is used as an oxidizing agent it is nearly always reduced to NO in which we see that the nitrogen has a polarity-value of +2. Hence each molecule of nitric acid when reduced to NO furnishes three bonds to the reducing agent.



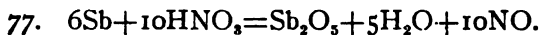
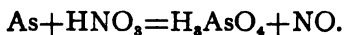
Here each phosphorus atom gains 5 bonds so that we take 5 molecules of nitric acid, and as each molecule of the acid furnishes 3 bonds we take 3 atoms of phosphorus, for  $3 \times 5 = 5 \times 3$ . The total number of units of polarity-value transferred is 15. The five molecules of nitric acid must, of course, give five molecules of NO, and the three atoms of phosphorus form three molecules of phosphoric acid requiring nine hydrogen atoms of which the  $5\text{HNO}_3$  furnish only five so that three molecules of water must be added to the factors.

[It is quite practicable to apply the rule to the same equation if molecules of phosphorus be written instead of atoms. The molecule of phosphorus is tetratomic and, therefore, the equation would be:

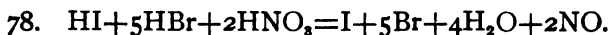


76. The student may now apply the rule to the following equation and balance it in the same manner as the preceding one (Ex.

75) for the structure of arsenic acid is quite analogous to that of phosphoric acid:

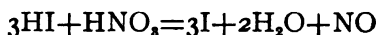


The antimony gains 5 bonds, so that the *proportions* of the factors must be  $3\text{Sb} + 5\text{HNO}_3$ ; but as the  $\text{Sb}_2\text{O}_5$  requires an even number of antimony atoms the numbers 3 and 5 must be multiplied by 2.

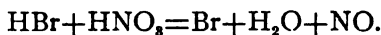


Here we have two different reactions combined and we find that 1 unit is gained by the iodine and 5 units by the 5 bromine atoms; these 6 units of polarity-value are furnished by the  $2\text{HNO}_3$ .

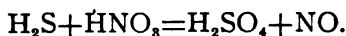
The student may now examine:



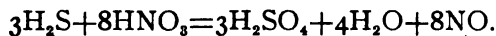
and balance the following:



79. Hydrogen sulphide and nitric acid react upon each other to form sulphuric acid and NO. We write



To balance this equation we write 8 before the  $\text{HNO}_3$  because the sulphur atom of the  $\text{H}_2\text{S}$  gains 8 units of polarity-value since its polarity-value is changed from  $-2$  to  $+6$ , a difference of 8 units; and we write 3 before the  $\text{H}_2\text{S}$  because the N of the  $\text{HNO}_3$  loses 3 bonds. Our factors, then, must be  $3\text{H}_2\text{S} + 8\text{HNO}_3$ , and we can readily see that the products must accordingly include 4 molecules of  $\text{H}_2\text{O}$ , so that the finished equation is:

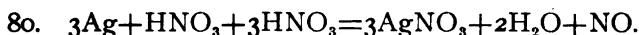


It will be seen that the polarity-value of the sulphur is reversed. We should, therefore, expect to find that the *arithmetical* sum of the positive bonds of the factors is not the same as the arithmetical sum of the positive bonds of all the products together, and as

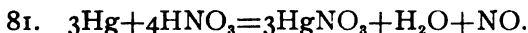
the number of bonds of the three sulphur atoms of the  $3\text{H}_2\text{S}$  is 6 (six negative bonds) the difference between the number of the positive bonds of the factors and of the positive bonds of the products must be 6. This, the student will find, is the case. The same difference, of course, appears between the sums of the negative bonds of factors and products. The factors show 54 positive and 54 negative bonds, but the products show only 48 positive and 48 negative bonds in actual combination.

The only elements which have changed their valence are, of course, the sulphur and the nitrogen—i. e., the reducing element and the oxidizing element. In the factors we find 6 negative sulphur bonds and 40 positive nitrogen bonds; in the products we find 18 positive sulphur bonds and 16 positive nitrogen bonds, but no negative bonds of either sulphur or nitrogen. But the algebraic sum of  $-6$  and  $+40$  is  $+34$ , and that is also the sum of  $+18$  and  $+16$ .

. In examples 75 to 79 inclusive the nitric acid employed is all consumed as an oxidizing agent. But when metals are dissolved in nitric acid forming metallic nitrates we use the acid for two purposes: first, for the oxidation; and, second, to form the nitrate. This will be illustrated in examples 80 to 84.

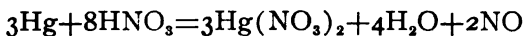


The first molecule of  $\text{HNO}_3$  is required for the oxidation and suffices to furnish the 3 bonds required by 3 silver atoms to form silver salt. The  $3\text{HNO}_3$  enter into the formation of the  $3\text{AgNO}_3$ .



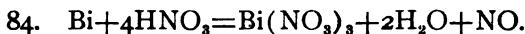
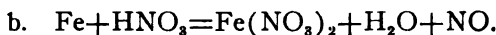
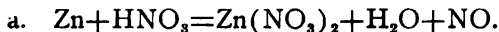
Mercurous mercury is, like silver, a monad. Hence this equation is analogous to the preceding one.

82. When mercuric nitrate is formed by the solution of mercury in nitric acid the reaction is:

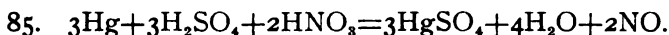


for mercuric mercury is a dyad. The 3 mercury atoms gain 2 bonds each so that 2 molecules of nitric acid must be required for the oxidation. The other six molecules form the nitrate.

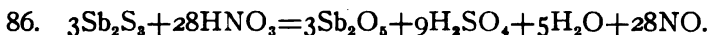
83. The student can complete the following equations:



Here one molecule of nitric acid is required to furnish the 3 bonds which the bismuth acquires.



The three mercury atoms take 6 bonds from the nitrogen of the two molecules of nitric acid.



Two elements—the antimony and the sulphur—are here oxidized. Each antimony atom gains 2 and each sulphur atom gains 8 units of polarity-value, so that the two antimony atoms and three sulphur atoms of each molecule of  $\text{Sb}_2\text{S}_3$  gain together 28 units; hence we take 28 molecules of  $\text{HNO}_3$ ; and as each molecule of  $\text{HNO}_3$  furnishes 3 bonds we write 3 before the  $\text{Sb}_2\text{S}_3$ .

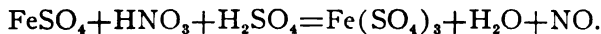


The mercury atom gains 1 unit and each iodine atom gains 6 units. Hence we take 7 molecules of nitric acid for the oxidation of the Hg and I of 3 molecules of  $\text{HgI}$ . The additional 6 molecules of nitric acid are consumed in forming the mercuric nitrate.

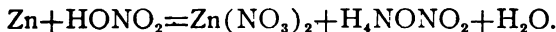


One molecule of nitric acid suffices to furnish an additional bond to each of the three iron atoms.

89. The student may complete the following equation:



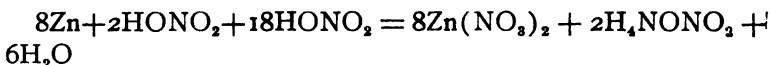
90. When zinc is dissolved in cold dilute nitric acid the products formed are zinc nitrate and ammonium nitrate. The equation representing this reaction is:



I have here written the molecule of nitric acid as  $\text{HONO}_2$  in-

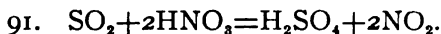
stead of  $\text{HNO}_3$  and the molecule of ammonium nitrate as  $\text{H}_4\text{NONO}_2$  in order to bring out more clearly the structure of the latter compound and the respective polarity-values of the two nitrogen atoms it contains, for the first nitrogen atom in  $\text{H}_4\text{NONO}_2$  has a polarity-value of  $-3$  (although its "valence" is 5) while the second nitrogen atom has a polarity-value of  $+5$ .

To balance this equation we must have 2 molecules of nitric acid for the zinc as each atom of the metal gains 2 bonds; and we write 8 atoms of zinc because the nitrogen which changes its polarity-value from  $+5$  to  $-3$  loses 8 units. But as 8 atoms of zinc form 8 molecules of nitrate, and the two molecules of nitric acid which furnished the bonds to the zinc formed the ammonium radical for two molecules of ammonium nitrate it is evident that 18 additional molecules of nitric acid are necessary for the formation of the two nitrates, so that the rule would lead to the equation:



which we can reduce to its lowest terms by using the common divisor 2.

In some reactions where nitric acid is used as an oxidizing agent the acid is reduced to  $\text{NO}_2$  instead of  $\text{NO}$ , and in other cases it is reduced to  $\text{N}_2\text{O}_3$ . Examples of such reactions are as follows:

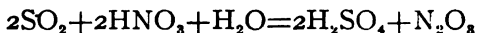


As the sulphur gains 2 bonds each molecule of nitric acid in this case furnishes but one bond.

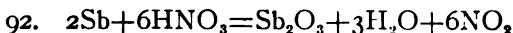
But when water is present and the supply of nitric acid less abundant the reaction may be:



Or the reaction may be represented as:



which is a combination of the other two.



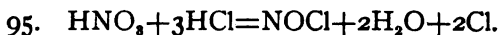
shows that the Sb gains 3 bonds, and the N of the  $\text{HNO}_3$  loses only 1. But as  $\text{Sb}_2\text{O}_3$  contains 2 antimony atoms it is necessary to double the numbers found by the rule.



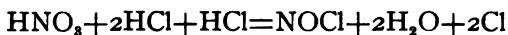
The complex structure of  $\text{H}_{10}\text{Sn}_5\text{O}_{15}$  is doubtful. It is called "metastannic acid," but is a polymeric form of  $\text{H}_2\text{SnO}_3$ , which is clearly monometastannic acid.



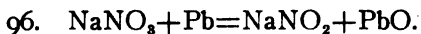
is an equation showing how nitric acid can be reduced by nascent hydrogen so as to form ammonium nitrate. As the nitrogen atom loses 8 units of polarity-value the reduction requires 8 hydrogen atoms. See Ex. 90.



The N of the  $\text{HNO}_3$  loses 2 units, and these are gained by the two chlorine atoms which are liberated. The rule would give us



for the additional molecule of HCl is required to form the nitrosyl chloride.

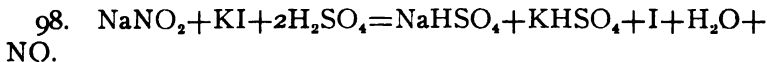


Here the N gives up 2 units to the Pb.



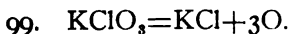
The two atoms of arsenic take 4 bonds from the two molecules of  $\text{NaNO}_3$ .

**444.** *Nitrites may also serve as oxidizing agents:*



The iodine takes 1 unit of polarity-value from the nitrogen.

**445.** *Oxidation by chlorates.*



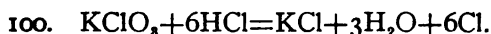
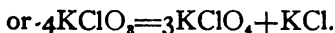
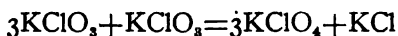
The rule would give us



which we reduce to its lowest terms.

Each chlorine atom loses 6 units, and each oxygen atom gains 2 units of polarity-value; as there are three oxygen atoms in each molecule of  $\text{KClO}_3$  it will be seen that the chlorine of one molecule gives up 6 units of polarity-value to the three oxygen atoms for the polarity-value of the Cl in  $\text{KClO}_3$  it is +5 and in  $\text{KCl}$  it is -1.

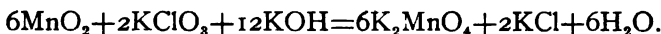
The student will, from the foregoing, readily explain the following:



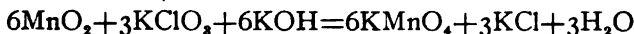
Here the six chlorine atoms are released from the  $6\text{HCl}$  by the six units of polarity-value transferred to them by the chlorine of the  $\text{KClO}_3$ .



As the manganese atom gains 2 units and the chlorine atom loses 6 units the rule would give us



In this reaction the manganese atom gains 3 units, so that the rule would give



which we reduce to its lowest terms in the usual way.

103. To balance the equation—



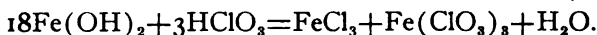
we first identify the iron as the reducing agent and the chlorine as the oxidizing agent. The iron atom gains 1 positive bond;

each chlorine atom acting as an oxidizing agent gives up 6 units of polarity-value.

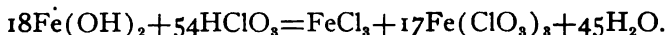
That would give us—



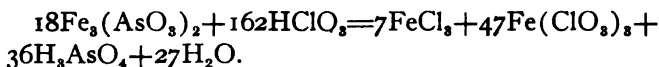
But all of the chlorine which acted as an oxidizing agent entered into the formation of the  $\text{FeCl}_3$  which contains three atoms of chlorine, whereas the  $\text{HClO}_3$  contains only one. It is therefore necessary to multiply the oxidizing and reducing agents by 3. We then get—



Now, as only one molecule of  $\text{FeCl}_3$  can be formed out of the  $3\text{HClO}_3$ , it follows that 17 molecules of  $\text{Fe}(\text{ClO}_3)_3$  must be formed, which require 51 additional molecules of  $\text{HClO}_3$ . Hence the finished equation will be:

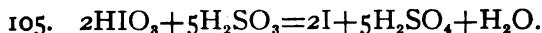


104. The student may now examine and explain the following equation:



The transfer of polarity-value requires 7 molecules of  $\text{HClO}_3$  for every 6 molecules of the  $\text{Fe}_3(\text{AsO}_3)_2$ , because each iron atom gains 1 bond and each arsenic atom gains 2 bonds, so that all the atoms of iron and arsenic of each molecule of ferrous arsenite gain together 7 bonds. This explains why seven molecules of  $\text{FeCl}_3$  must be obtained. (See Ex. 103.)

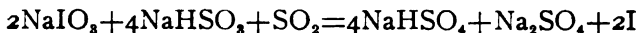
**446.** *Oxidation by iodates.*



In this equation it is shown that the iodine atom of  $\text{HIO}_3$  has a polarity-value of +5 and that the sulphur atom of the  $\text{H}_2\text{SO}_3$  has a value of +4. Ten units of polarity-value are transferred from the iodine to the sulphur.

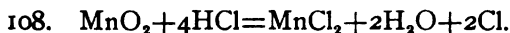
106. In  $\text{NaIO}_3 + 3\text{NaHSO}_3 = 3\text{NaHSO}_4 + \text{NaI}$  the iodine gives 6 units of polarity-value to the sulphur atoms.

107. In the equation

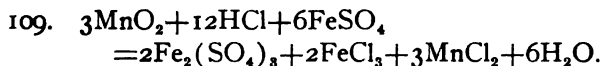


the iodine is reduced from the polarity-value of +5 to one of 0, and the sulphur atoms of both the  $\text{NaHSO}_3$  and the  $\text{SO}_2$  are oxidized from a polarity-value of +4 to one of +6. The two iodine atoms together give up 10 units to the five sulphur atoms. Under the rule the proportions of the oxidizing agent and reducing agent must be as 2 to 5. But in this case the five sulphur atoms which are oxidized are contained in two different kinds of molecules. The proportions required of  $\text{NaHSO}_3$  and  $\text{SO}_2$  are known from the fact that the  $2\text{NaIO}_3$  must furnish the sodium that forms  $\text{Na}_2\text{SO}_4$ , and hence only one molecule of that salt can be formed, so that only one molecule of  $\text{SO}_2$  is required.

**447.** *Oxidation by manganese dioxide.*



The manganese loses two units of polarity-value, which are taken up by the two liberated chlorine atoms. Four molecules of  $\text{HCl}$  are required instead of two because  $\text{MnCl}_2$  is formed.

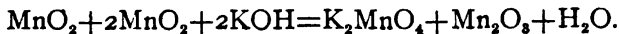


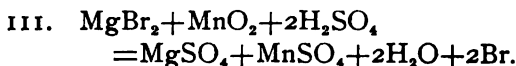
As the manganese atom of  $\text{MnO}_2$  gives up 2 bonds and the iron atom of the  $\text{FeSO}_4$  gains 1 bond, the proportions of the oxidizing agent and reducing agent must be  $\text{MnO}_2 + 2\text{FeSO}_4$ . But ferric sulphate is one of the products, and this requires the sulphate radical ( $\text{SO}_4$ ) three times in each molecule. We therefore multiply the  $\text{MnO}_2 + 2\text{FeSO}_4$  by 3, which will give us  $3\text{MnO}_2 + 6\text{FeSO}_4$ , from which we see that three molecules of  $\text{MnCl}_2$  and two molecules of  $\text{Fe}_2(\text{SO}_4)_3$  must be formed, leaving two iron atoms to form ferric chloride. Twelve molecules of  $\text{HCl}$  are required for the formation of  $2\text{FeCl}_3$  and  $3\text{MnCl}_2$ ; hence 6 molecules of water will also be formed.

110. In the equation

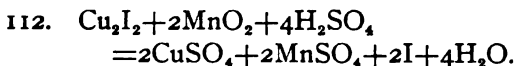


one manganese atom gains 2 bonds and these are furnished by the other two atoms of the same element. The rule gives us

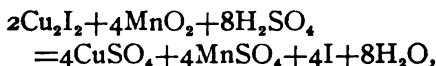




Here the two bromine atoms gain 2 units of polarity-value furnished by the manganese.

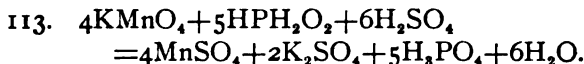


We find here that each copper atom gained 1 bond and each iodine atom also 1 bond; hence the rule gives us

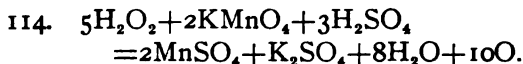


which can be divided by 2.

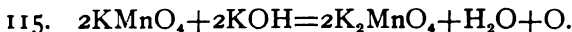
**448.** *Oxidation by potassium permanganate.*



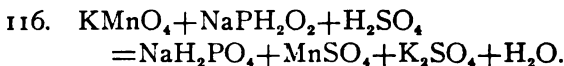
The Mn is reduced from a polarity-value of +7 to one of +2, losing 5 bonds; the P is oxidized from a polarity-value of +1 to one of +5, gaining 4 bonds. Thus 20 positive bonds are transferred ( $4 \times 5 = 20$ ).



Each atom of Mn is reduced from a polarity-value of +7 to one of +2, losing 5 bonds; the 2 atoms of Mn thus lost 10 bonds. What became of them?

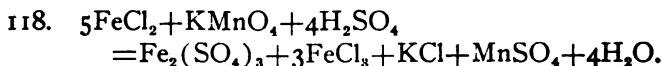
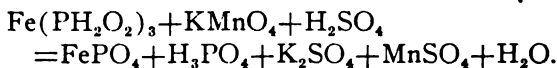


Here the Mn loses only 1 unit, while the oxygen gains 2; 2 units are transferred.

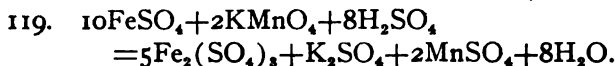


This equation is not balanced. The student will please balance it on the principle applied in Ex. 113.

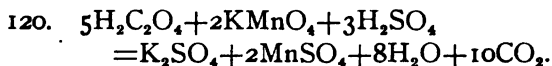
117. The student may now complete or balance this:



The reducing agent is  $\text{FeCl}_2$ . Each iron atom gains 1 bond and the manganese loses 5 bonds.



This equation will be understood from Ex. 118.



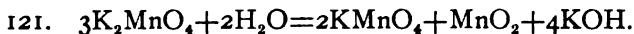
The carbon atoms of the molecule  $\text{H}_2\text{C}_2\text{O}_4$  have together a polarity-value of +6, for the four oxygen atoms have eight negative bonds and the two hydrogen atoms have two positive bonds. In the  $\text{CO}_2$  the carbon has four positive bonds. Hence the two carbon atoms gained 2 units and for the 2 atoms we take 2 molecules of  $\text{KMnO}_4$ .

The carbon atoms of the  $\text{H}_2\text{C}_2\text{O}_4$  are tied to each other for the structure of the molecule is

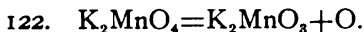


from which it will be seen that one of the carbon atoms has a polarity-value of +4, while the other has a polarity-value of +2.

**449.** *Oxidation by potassium manganate.*

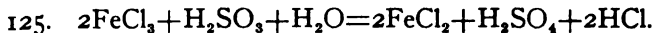
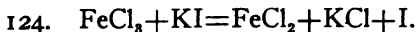


Here two molecules of  $\text{K}_2\text{MnO}_4$  form two molecules of  $\text{KMnO}_4$ , the Mn of each molecule gaining 1 bond; the 2 bonds required for this oxidation come from the Mn of the third molecule of  $\text{K}_2\text{MnO}_4$  which forms  $\text{MnO}_2$ .



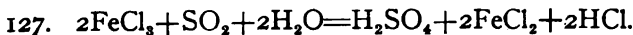
The Mn is reduced from a polarity-value of +6 to one of +4; the oxygen atom gained the 2 units lost by the Mn.

**450.** *Oxidation by ferric chloride.*

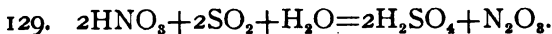
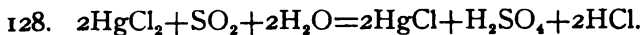
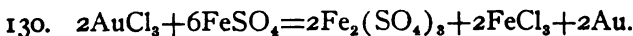
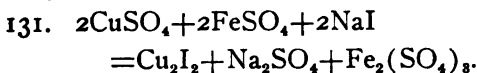
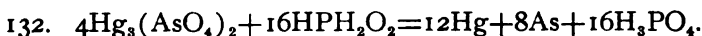
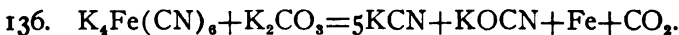
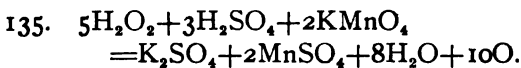
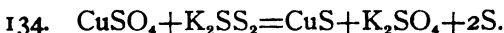
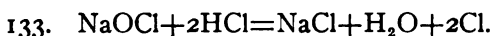


126. The student may complete the equation:

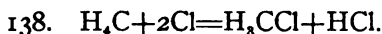


**451.** *Reduction by sulphur dioxide.*

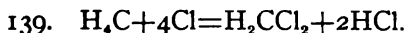
(See Ex. 125.)

**452.** *Reduction by ferrous sulphate.*Why not one molecule of  $\text{AuCl}_3$  and three  $\text{FeSO}_4$ ?**453.** *Reduction by hypophosphorous acid.***454.** *Miscellaneous examples.*

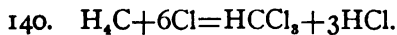
**455.** A few reactions from organic chemistry which are of special interest to pharmacists will serve to further elucidate the conception of chemical polarity, the principle of balancing the units of positive and negative combining value, and the transfer of units of polarity-value:



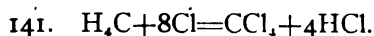
The carbon in  $\text{H}_4\text{C}$  has clearly a polarity-value of  $-4$ ; in  $\text{H}_2\text{CCl}$  its polarity-value is  $-2$ .



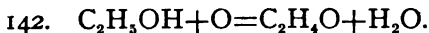
The polarity-value of the carbon atom is here changed from  $-4$  to  $0$ , a difference of  $4$  units.



Here the carbon atom gains  $6$  units.

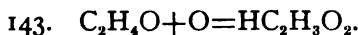


The difference between the polarity-value of the carbon in  $\text{H}_4\text{C}$  and in  $\text{CCl}_4$  amounts to 8 units.

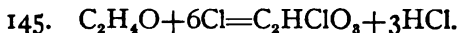


In this equation we find that the algebraic sum of the units of polarity-value of the two carbon atoms in the  $\text{C}_2\text{H}_5\text{OH}$  is  $-4$ , while in the  $\text{C}_2\text{H}_4\text{O}$  it is  $+2$ .

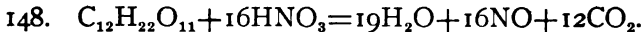
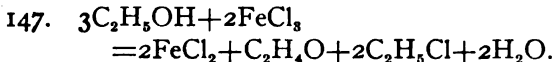
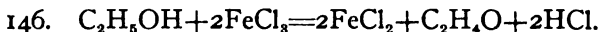
[The algebraic sum of the units of polarity-value of all the atoms of any one element in any compound molecule is the difference between 0 and the algebraic sum of the units of polarity-value of all the other atoms in the same molecule (par. 195). Hence the algebraic sum of the units of polarity-value of the two carbon atoms in  $\text{C}_2\text{H}_5\text{OH}$  is  $-4$  because the algebraic sum of the units of polarity-value of the six hydrogen atoms and one oxygen atom contained in the same molecule is  $+4$ . The algebraic sum of the units of polarity-value of the two carbon atoms in  $\text{C}_2\text{H}_4\text{O}$  is  $+2$  because the algebraic sum of the polarity-units of the  $\text{H}_4\text{O}$  of the same molecule is  $-2$ .]



The algebraic sum of the units of polarity-value of the carbon atoms is  $-2$  in  $\text{C}_2\text{H}_4\text{O}$ , but in  $\text{HC}_2\text{H}_3\text{O}_2$  it is 0.

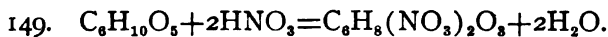


The algebraic sum of the carbon bonds in the chloral,  $\text{C}_2\text{HClO}_3$ , is  $+4$ , because the algebraic sum of all the positive and negative bonds of the other atoms is  $-4$ .

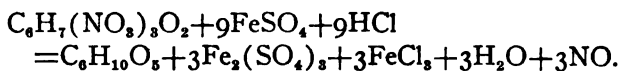


The algebraic sum of the units of polarity-value of the 12 carbon bonds in the  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  is 0, because the hydrogen bonds and oxygen bonds are equal numbers. All the carbon forms  $\text{CO}_2$ , so that the 12 carbon atoms each gain 4 bonds, or they gain 48 bonds together; the N of the  $\text{HNO}_3$  loses 3 bonds. Hence the rule requires three molecules of  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  and 48 molecules of

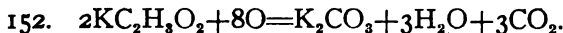
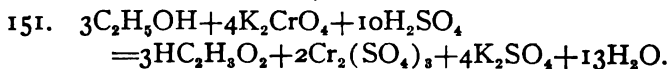
$\text{HNO}_3$ , but we can reduce those numbers by the common divisor 3.



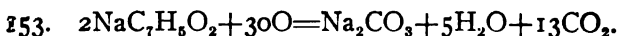
Upon examination the student will find that no oxidation and reduction can be found in this equation, for the polarity-values of all the elements remain unchanged. But oxidation and reduction may be discovered in—



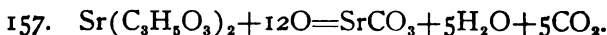
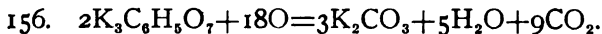
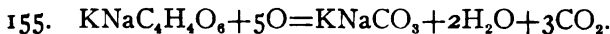
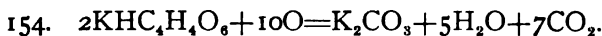
The three carbon atoms of each molecule of  $\text{C}_3\text{H}_5(\text{OH})_3$  have together the polarity-value of  $-2$ ; but three carbon atoms in three molecules of  $\text{CO}_2$  (all the carbon forms  $\text{CO}_2$ ) have together a polarity-value of  $+12$ . The difference between  $-2$  and  $+12$  is 14.



The two carbon atoms of the potassium acetate have a polarity-value of 0; in the products each of these carbon has a value of  $+4$ .



The algebraic sum of the units of polarity-value of all the carbon atoms of one molecule of  $\text{NaC}_7\text{H}_5\text{O}_2$  is  $-2$ ; but the polarity-value of all the seven carbon atoms in the products is 28; the difference is 30.



## CHAPTER XXV.

### ATOMIC POLARITY-VALUE AS AN AID TO THE DETERMINATION OR VERIFICATION OF INTERATOMIC LINKING OR THE STRUCTURE OF MOLECULES.

**456.** The examples of reactions of oxidation and reduction presented in Chapters XXI to XXIV, inclusive, furnish conclusive evidence that chemical polarity and atomic valence are real properties of *combined* atoms and that their joint expression (called polarity-value in this book) rests upon as firm ground as that supporting the atomic hypothesis. It is apparent that no reaction accompanied by any change in the valence of any atom can occur except in strict obedience to the law that **the total number of units of polarity-value of all atoms of all matter is a constant number (=zero)**, and that a gain of polarity-value by one or more atoms must, therefore, inevitably be attended by an exactly corresponding loss by another atom or other atoms.

Assuming that no two atoms, whether of the same element or of different elements, can be linked together in chemical combination unless they are of opposite chemical polarity with respect to each other, that the hydrogen atom in combination with any other element invariably has a polarity-value of  $+1$ , and that the polarity-value of the oxygen atom in combination with any other element is invariably  $-2$ , we are at once in possession of the means whereby we can determine the algebraic sum of the units of polarity-value of any third element in combination with hydrogen and oxygen in any ternary molecule. If we also know the valence of that third element, it follows that we may with the aid of these data ascertain the possible structures of comparatively simple ternary molecules, for molecular formulas which are clearly inconsistent with the hypotheses of polarity, valence, and polarity-value can not be true.

We have already pointed out elsewhere that there can be no such compound as a "calcium pentasulphide" represented by the molecular formula  $\text{CaS}_5$ , because such a formula is inconsistent with the conception of polarity-value. All sulphides contain

negative sulphur having a polarity-value of  $-2$ ; but the calcium atom can not have a polarity-value of  $+10$  for no atom of any kind can have a greater polarity-value than  $+8$ . Moreover, it is impossible to balance the equation

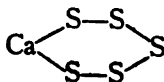


by the application of the principles set forth in Chapter XVIII, and any chemical equation involving oxidation and reduction which can not be balanced by the rules there given can not be right. But the equation—



is right and consistent with the theory of polarity-value.

a. The empiric formula  $\text{CaS}_5$  truly represents the percentage composition of the substance erroneously called calcium penta-sulphide. But as the calcium atom can not be linked to all of the sulphur atoms *directly*, the compound can not be a sulphide at all. That the calcium atom has a polarity-value of  $+2$  is well known; from this it necessarily follows that the algebraic sum of the units of polarity-value of the five sulphur atoms together must be  $-2$ , and this proves that one or more sulphur atoms must possess positive polarity. If we assume that *one* sulphur atom is positive, then that one sulphur atom must have a polarity-value of  $+6$ , since the algebraic sum of the units of polarity-value of the remaining four sulphur atoms must be  $-8$ , and the algebraic sum of the units of polarity-value of all five must be  $-2$ . This leads us at once to the formula  $\text{CaSS}_4$ , or  $\text{CaS}_2\text{SS}_2$ . If we assume that two of the sulphur atoms are positive, then each of these must have a polarity-value of  $+2$  in order to agree with the established fact that in  $\text{CaS}_5$  the algebraic sum of all the five sulphur atoms must be  $-2$ . But the structure



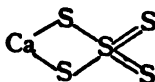
which is the only one possible on the assumption that two of the sulphur atoms (those intermediate between the other sulphur atoms) have each two positive bonds, is an altogether improbable one because bivalent positive sulphur, performing the

acidic function in a sulphur salt of calcium, would naturally form the hypothiosulphite  $\text{CaSS}_2$ , or  $\text{CaSSS}$ , in which only one sulphur atom is positive.

The calcium atom of  $\text{CaS}_6$ , being a positive dyad, can not be united to only one of the sulphur atoms because the result would be a saturated molecule  $\text{CaS}$ , excluding the other four sulphur atoms from possible connection; it is, therefore, linked to two negative sulphur atoms forming the radical

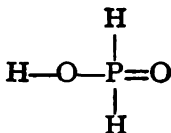


The structural formula

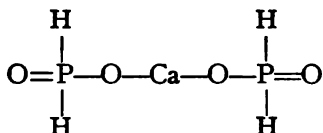


is, therefore, the most rational one, because it is not only in harmony with the theory of atomic linking in accordance with the conception of atomic polarity-value, but it corresponds clearly to the structure of  $\text{CaSO}_4$ . The compound is, therefore, calcium tetrathiosulphate.

b. The empiric formula  $\text{PH}_3\text{O}_2$  or  $\text{H}_3\text{PO}_2$  represents hypophosphorous acid. As it shows 3 (positive) hydrogen bonds and 4 (negative) oxygen bonds, it follows that the polarity-value of the P must be  $+1$ . As we know the compound to be a monobasic hydroxyl acid the only structural formula consistent with the facts must be

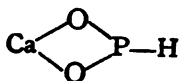


The empiric formula  $\text{CaP}_2\text{H}_4\text{O}_4$ , or  $\text{CaH}_4\text{P}_2\text{O}_4$ , stands for calcium hypophosphite; the corresponding structural formula must be

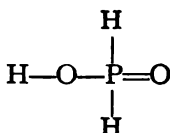


because the calcium atom is a positive dyad and each phosphorus atom must accordingly have the polarity-value  $+1$ . If hypo-

phosphorous acid were  $(\text{HO})_2\text{PH}$ , then calcium hypophosphite would be

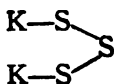


but as its actual percentage composition leads to the empiric formula  $\text{CaP}_2\text{H}_4\text{O}_4$  the structural formula must be in accord with that, and the structural formula of hypophosphorous acid must be

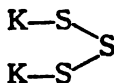


The phosphorus atom is a pentad here; but its polarity-value is  $+1$ .

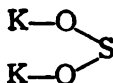
c. The empiric formula  $\text{K}_2\text{S}_3$  leads to the structural formula  $\text{K}_2\text{S}_2\text{S}$ , or  $\text{KSSSK}$ , or



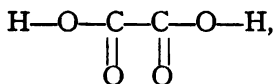
for there can be no di-potassium tri-sulphide,  $\text{K}_2\text{S}_3$ , since the invariable polarity-value of  $\text{K}$  is  $+1$  and the invariable polarity-value of *negative* sulphur is  $-2$ , but the formula



is not only in harmony with the conception of atomic polarity-value but a quite rational structure, being the normal hypothio-sulphite of potassium, corresponding to the hyposulphite



d. The empiric formula of oxalic acid is  $\text{CHO}_2$ ; but as it is known to be bibasic, containing two basic hydrogen atoms, we must double that formula, making it  $\text{C}_2\text{H}_2\text{O}_4$ . We find that the algebraic sum of the units of polarity-value of the two carbon atoms must here be  $+6$ , and the only structural formula compatible with that value is



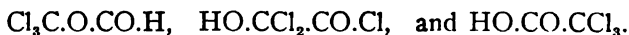
which we know to be correct because the molecule contains COOH (or HOCO) twice. The two carbon atoms are linked together by a positive bond from one and a negative bond from the other; these two bonds, therefore, cancel each other and leave 6 positive carbon bonds all of which must be united to the negative oxygen atoms.

e. The empiric formula of acetic acid is  $\text{CH}_3\text{O}$ . But we know that it is a monobasic organic acid and that its replaceable hydrogen atom is that of the hydroxyl group united to CO, or, in other words, that this acid contains HOCO (or COOH). Hence the empiric formula must be doubled,  $\text{C}_2\text{H}_4\text{O}_2$ . The vapor density proves that the formula  $\text{C}_2\text{H}_4\text{O}_2$  is correct.

Three different structural formulas are possible, all of which agree with the empiric formula  $\text{C}_2\text{H}_4\text{O}_2$ . Those three formulas are  $\text{H}_3\text{C.O.CO.H}$ ,  $\text{HO.CH}_2\text{.CO.H}$ , and  $\text{HO.CO.CH}_3$ . It will be seen, therefore, that the true interatomic linking can not be determined from the respective polarity-values of the component atoms *without any other aids*; and as acetic acid is known to contain OCOH the true structural formula can in this case be no other than  $\text{HO.CO.CH}_3$ . Nevertheless this example does not disprove the utility of polarity-value as an aid in the confirmation of the correctness of structural formulas.

f. The empiric formula of ethyl alcohol, and of methyl ether, is  $\text{C}_2\text{H}_6\text{O}$ . The two carbon atoms must here have 6 negative and 2 positive bonds, for their total number is 8 and the algebraic sum of their units of polarity-value is seen to be  $-4$ . The only two structural formulas that can be derived from this empiric formula are  $\text{H}_3\text{C.O.CH}_3$  (methyl ether) and  $\text{H}_3\text{C.CH}_2\text{.OH}$  (ethyl alcohol), for these are the only formulas in which the atomic linking is consistent with the hypotheses of polarity and valence.

g. Trichloroacetic acid is  $\text{C}_2\text{HO}_2\text{Cl}_3$ . Three different structural formulas are possible which correspond to  $\text{C}_2\text{HO}_2\text{Cl}_3$ , namely:

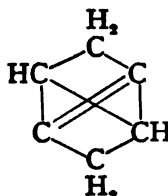
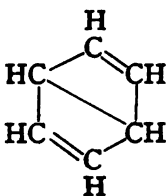
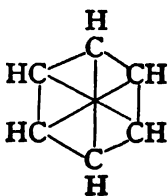
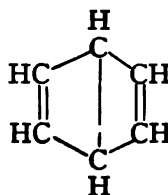
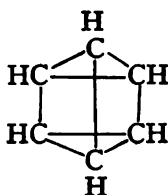
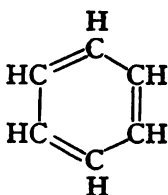


In all of these formulas it will be seen that the algebraic sum of the units of polarity-value of the two carbon atoms must be +6, for 7 of the carbon bonds are positive, while the eighth is negative. The correct structural formula is, of course, the last one for the compound, being an acid, must contain  $\text{OC.OH}$ ; but the first formula is practically identical with the third.

h. The empiric formula of the molecule of methyl alcohol is  $\text{CH}_4\text{O}$ . The carbon atom here has the polarity-value  $-2$ , and the only possible structural formula agreeing with it is  $\text{H}_3\text{C.OH}$ .

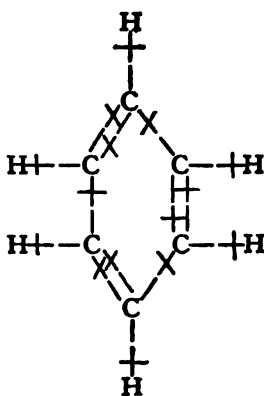
i. In aldehyde,  $\text{C}_2\text{H}_4\text{O}$ , the algebraic sum of the units of polarity-value of the two carbon atoms must be  $-2$ . In other words, 5 of the 8 carbon bonds are negative and the other 3 are positive. It is evident that in this molecule the two carbon atoms must be linked to each other as the single oxygen atom can not cancel more than two of the three positive carbon bonds. The only possible structural formula, therefore, is  $\text{H}_3\text{C.CO.H}$ .

j. The molecular formula of benzene is  $\text{C}_6\text{H}_6$ . The algebraic sum of the units of polarity-value of the 6 carbon atoms must here be  $-6$ . The total number of carbon bonds is 24. Hence 15 of the carbon bonds must be negative and the other 9 positive. Therefore, 9 negative carbon bonds are canceled by the 9 positive carbon bonds, while the remaining 6 negative carbon bonds are linked to the 6 hydrogen atoms. As the hydrogen atoms can not be linked to each other, it follows that all of the 6 carbon atoms must be linked together in one of several possible ways:

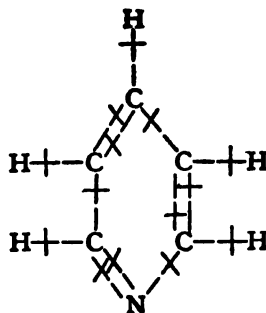


The first of these formulas was proposed by Kekulé, the second by Claus and Kerner, the third by Dewar, the fourth by Ladenburg. Still other formulas are possible. But the generally accepted structural formula of benzene is that of Kekulé.

k. Assuming that Kekule's formula for benzene is the right one we may now attempt to indicate the respective polarities of the several bonds which we shall do by using a cross (+) to represent positive bonds and a straight line (—) to indicate the negative bonds. We will at the same time write the probable structural formula for pyridine in the same manner so as to show their relationship to each other:



Benzene.



Pyridine.

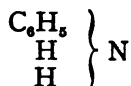
It will be seen here that the trivalent negative nitrogen has replaced the trivalent negative group CH, and as the formula shows pyridine to be a saturated molecule in the sense that all of the bonds of its atoms are tied and the requirements of polarity and actual valence satisfied, the student may not readily see how this molecule can become linked to the molecule of an acid to form a salt. But while the N has only three bonds in the pyridine, and all of them are negative, we must remember that in  $H_2N$ , too, the nitrogen is a negative triad, and that the N of the pyridine as well as that of ammonia can acquire two additional bonds *without changing its polarity-value*, so that we have—



The  $\text{C}_6\text{H}_5\text{NHCl}$  may be seen to be  $\text{C}_6\text{H}_5\text{N} \begin{array}{l} \text{H} \\ \diagup \\ \text{Cl} \end{array}$  if we admit that

$\text{H}_3\text{NHCl}$  is really  $\text{H}_4\text{NCl}$ . The triad nitrogen atom with its polarity-value of  $-3$  in the pyridine molecule separates the hydrogen and chlorine of the  $\text{HCl}$  from each other by acquiring an additional negative bond to hold the hydrogen and a positive bond to hold the chlorine, but the pentad nitrogen of the pyridine hydrochloride still has a polarity-value of  $-3$  just as the pentad N of  $\text{H}_4\text{NCl}$  has the same polarity-value.

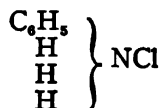
Aniline is  $\text{C}_6\text{H}_5\text{NH}_2$ , or rather



Aniline hydrochloride is usually written



but it is undoubtedly



for any other system of atomic linking is impossible. The nitrogen of aniline hydrochloride as well as of aniline itself has a polarity-value of  $-3$  although it is a triad in the aniline and a pentad in the salt. The same rule applies to all the salts of ammonia, aniline, pyridine, quinoline, and all other organic bases built on the ammonia type. It is not improbable that all alkaloidal salts are formed in the same manner, i. e., by a rearrangement of the atomic linking such as results from a change in the valence of the nitrogen unaccompanied by any alteration of its polarity-value, the "replaceable hydrogen" of the acid being thereby separated from the acid molecule and attached to the nitrogen by one of the new bonds of that element (instead of being replaced)

while the "acid-residue" is also linked to the same nitrogen atom by its other new bond. The change of valence of the nitrogen in these reactions must be due to the predisposing tendency of the acid and the base to saturate each other.

1. Cyanogen, CN, can not but be a negative radical for carbon is a tetrad and hydrocyanic acid is HCN and not CNH; for although the nitrogen atom can be a pentad and can exercise negative polarity toward hydrogen while it exercises positive polarity toward carbon, or oxygen, or chlorine, it is extremely improbable that the carbon atom in CNH can have two positive and two negative bonds (a polarity-value of 0) and it is certain that the N can not have a polarity-value of  $-5$  in any case. Hence the unused or potential combining unit of CN is a carbon bond—not a nitrogen bond.

But the bond by which  $H_4N$  is united to a negative atom is, of course, a nitrogen bond, and the two potential valence units of  $H_4N$  belong to the nitrogen atom and must be one of them negative and the other positive.

## CHAPTER XXVI.

### THE PERIODICITY OF PROPERTIES OF THE ELEMENTS.

**457.** The classification of the chemical elements into natural divisions and groups is attended with difficulty because the properties of one group merge into those of other groups.

Their division into metallic elements and non-metallic elements has been fully discussed in Chapter IV, and attention called to the fact that several elements possessing the characteristic physical properties of metals (as, for instance, tin and antimony) do not possess the chemical properties of other and more decidedly metallic elements but do instead resemble the non-metallic elements in very important respects.

Various methods of classification suggest themselves, based upon valence, polarity, acidic and basic functions, atomic weights, atomic volumes, relative chemical combining energy, and other properties. A general division of the metallic elements into "light metals" and "heavy metals" carries with it some advantages. Certain families of elements are universally recognized as exhibiting well defined family traits, as, for example, the halogens, the sulphur group, the alkali metals, the calcium group, etc. Less definite groupings, like that of the "noble metals," have also been referred to for purposes of description.

But the most rational system of classification yet known is the so-called "Periodic System," based upon the recurrence of striking similarities of chemical behavior coincident with definite periods of increasing or decreasing atomic mass.

**458.** Newlands called attention to some decided evidences of the connection between the atomic weights and the chemical properties of the elements.

In 1868 Mendeleeff and Lothar Meyer, independently of each other, published tables of the elements arranged in periods in the order of their atomic weights to show that their classification into natural groups or families may be based upon such an arrangement.

This **Periodic System** of classification of the elements of matter according to their atomic weights and functions is intensely interesting, suggestive, and helpful to students of chemistry.

The most striking chemical properties of the elements concern their polarity and valence, and the character and structure of their compounds, and the periodic system of classification proves that there is a close relationship between these properties of the elements and their atomic weights and atomic volumes, and that the periodicity of the recurrence of the similarities of valence and functions obeys a natural law which is called the *Periodic Law* and which has been expressed as follows: "The chemical properties of the elements are periodic functions of their atomic weights."

**459.** When the elements having the lowest atomic masses beginning with lithium (hydrogen being at that time the only known element having an atomic mass lower than that of lithium) were arranged in order, ending with fluorine, the startling result was a "period" of seven elements whose respective ruling valences are 1, 2, 3, 4, 3, 2 and 1. This period of seven elements includes:

Li	Be	B	C	N	O	F
7	9	11	12	14	16	19

The student will see that the numbers placed below the symbols are the atomic masses. There are no other elements known whose atomic masses lie between 7 and 19. The period begins with an alkali metal and ends with a halogen. The element having the next higher atomic mass is sodium.

If now a second period of seven elements, in the order of their atomic weights, be set down, beginning with sodium, the seventh member of the period is again a halogen, and the respective ruling valences of these elements are, as before, 1, 2, 3, 4, 3, 2 and 1. This second period consists of:

Na	Mg	Al	Si	P	S	Cl
23	24.2	27	28.4	31	32	35.4

No other elements with atomic weights between 19 and 39 are known.

If polarity as well as valence be considered in connection with this second period of elements a still more striking result is brought out, namely, that the maximum polarity-values of these seven elements are +1, +2, +3, +4, +5, +6 and +7. The element next following chlorine in the order of increasing atomic mass is again an alkali metal, namely potassium.

A third period of seven elements, beginning with potassium, and including, as before, the next six elements in the regular order of their increasing atomic masses, is:

K	Ca	Sc	Ti	V	Cr	Mn
39	40	44	48	51.5	52	55

Although this period does not end with a halogen we find that the maximum polarity-values of these elements are, in their regular order, as before, +1, +2, +3, +4, +5, +6 and +7.

The elements next following manganese in the order of their atomic masses are iron, nickel and cobalt having, respectively, the atomic weights 56, 58.5 and 59; and the seventh element following manganese is not a halogen, nor an element having a maximum-polarity-value of +7. Here, then, is a break in the regular periodicity before noted.

But if the fourth period be made up of the seven elements ending with the next halogen, bromine, we get:

Cu	Zn	Ga	Ge	As	Se	Br
63.5	65.3	70	72.5	75.	79	80

The first member of this period of seven elements is not an alkali metal; but the evidences of the operation of the periodic law are still manifest for the respective polarity-values of these elements are again sufficiently in accord with the order before observed to warrant the conclusion that the apparent discrepancies or irregularities do not disprove the existence of the periodic law. The maximum polarity-values of the elements included in the period beginning with copper and ending with bromine are as follows:

Cu	Zn	Ga	Ge	As	Se	Br
+2	+2	+3	+4	+5	+6	+7

Copper apparently exercises a valence of  $+1$  in cuprous compounds; but the most stable salts of copper are those in which that metal acts as a dyad. Bromine has all the characteristics of the halogen group but compounds in which bromine exercises a polarity-value of  $+7$  are unknown.

Another period of elements beginning with the alkali metal rubidium which stands next after bromine in the magnitude of its atomic mass, is:

Rb	Sr	Y	Zr	Cb	Mo
85.5	87.5	89	90.5	93.5	96

and these six elements are closely related to K, Ca, Sc, Ti, V and Cr, while no element is now known which has an atomic weight between 96 and 100 and resembles Mn in valence and other properties.

A period of elements evidently corresponding to that beginning with copper and ending with bromine is formed by:

Ag	Cd	In	Sn	Sb	Te	I
108	112	114	119	120	125.5	126.5

The maximum polarity-values of these seven elements are unmistakably  $+1$ ,  $+2$ ,  $+3$ ,  $+4$ ,  $+5$ ,  $+6$  and  $+7$ , and the seventh member is a halogen.

Such results as these can not be accidental. It is, therefore, concluded that the chemical properties and atomic masses of the elements are governed by a universal law in accordance with which fundamental similarities of chemical behavior recur at regular intervals, or in periods, as the atomic mass increases.

The individuality of each element, however, can not be the resultant of its atomic mass and its chemical properties, but the reverse must be true—its atomic mass and properties are the attributes of its individuality which is the quality of the energy operating through it.

**460.** Mendeléeff's table is as follows:

Element	Group I.		Group II.		Group III.		Group IV.		Group V.		Group VI.		Group VII.		Group VIII.			
	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.				
1		H 1																
2	Li 7		Be 9		B 11		C 12		N 14		O 16		F 19					
3		Na 23																
4	K 39		Ca 40		Sc 44		Ti 48		V 51.5		Cr 52		Mn 55		Fe 59	Co 59	Cu 63.5	
5		(Cu) 63.5																
6	Rb 85.5		Sr 87.5		Y 89		Zr 90.5		Cb 98.5		Mo 96							
7		(Ag) 108																
8	Cs 133		Ba 137.5		La 138.5		Ce 139											
9																		
10									Ta 182.5		W 184							
11		(Au) 197																
12																		
		R <sub>2</sub> O		R <sub>2</sub> O <sub>2</sub>		R <sub>2</sub> O <sub>3</sub>		R <sub>2</sub> O <sub>4</sub>		R <sub>2</sub> O <sub>5</sub>		R <sub>2</sub> O <sub>6</sub>		R <sub>2</sub> O <sub>7</sub>	Highest oxides.			
							RH <sub>4</sub>		RH <sub>3</sub>		RH <sub>2</sub>		RH		Hydrogen compounds.			

It will at once be seen that there are many blank spaces in this table; but we may readily admit that the elements which fit into these spaces remain as yet undiscovered. The main principles of the arrangement are rigidly adhered to: the *known* elements are arranged in series in the order of their atomic weights, the alkali metals are placed in one column at the beginning of the even-numbered series and halogens at the end of each of the odd-numbered series of seven each. This arrangement leaves hydrogen as the only element set opposite series 1, and several heavy metals in group VIII outside the periods of seven.

But when Mendeleeff prepared his table there were a larger number of blank spaces in it. The elements scandium (Sc), gallium (Ga) and germanium (Ge) were then unknown. Nevertheless their existence was predicted by Mendeleeff who also correctly described their properties and stated their approximate atomic weights before they were discovered. The element uranium (U) did not then fit into this grouping according to the periodic system; but it was found that its supposed atomic weight was incorrect, and when the error had been corrected that element was readily assigned its natural position in the table.

The elements argon, helium, krypton, neon, samarium, erbium, terbium and others not yet sufficiently known, will undoubtedly in time be assigned their proper positions in harmony with the natural law which is so strikingly evident in the periodic system.

461. Lothar Meyer prepared a table in a similar manner showing that the elements may be arranged so as to form a spiral in which the last member of each period, *so far as the periods include an 8th group*, resembles the first member of the next period, as may be seen in the following exhibit based upon the various tables of Mendeleeff and Lothar Meyer. This table differs from the others only in that the periods are placed in a vertical position instead of horizontally, the ninth series is not omitted as in Meyer's table but is included as in Mendeleeff's, the polarity valences are indicated in the first column; and, at the foot of each column, is the symbol of the first element of the next period, showing how copper heads the period following immediately after that ending with nickel, while silver follows palladium and gold immediately succeeds platinum.

Series.												
Group	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
I. +1	H 1	Li 7	Na 23	K 39	+2 <i>Cu</i> 63.5	Rb 85.5	+2 <i>Ag</i> 108	Cs 133	.....	.....	+3 <i>Au</i> 197	.....
II. +2	.....	Be 9	Mg 24.2	Ca 40	<i>Zn</i> 65.3	Sr 87.5	<i>Cd</i> 112	Ba 137.5	.....	.....	+2 <i>Hg</i> 200	.....
III. +3	.....	B 11	Al 27	Sc 44	<i>Ga</i> 70	Y 89	<i>In</i> 114	La 138.5	.....	Yb 173	<i>Tl</i> 204	.....
IV. +4 -4	.....	C 12	Si 28	Ti 48	<i>Ge</i> 72.5	Zr 90.5	<i>Sn</i> 119	Ce 139	.....	.....	<i>Pb</i> 206.5	Th 232.5
V. +5 -3	.....	N 14	P 31	V 51.5	As 75	<i>Cb</i> 98.5	Sb 120	.....	.....	Ta 182.5	+3 Bi 208	.....
VI. +6 -2	.....	O 16	S 32	<i>Cr</i> 52	Se 79	<i>Mo</i> 96	Te 128	.....	.....	W 184	.....	U 238.5
VII. +7 -1	.....	F 19	Cl 35.4	<i>Mn</i> 55	Br 80	.....	I 126.5	.....	.....	.....	.....	.....
VIII.	.....	.....	.....	+6 Fe 56	.....	+8 Ru 101.5	.....	.....	.....	+8 Os 191	.....	.....
	.....	.....	.....	+4 Co 59	.....	+6 Rh 108	.....	.....	.....	+6 Ir 193	.....	.....
	.....	.....	.....	+2 Ni 59	.....	+4 Pd 107	.....	.....	.....	+4 Pt 195	.....	.....
		(Na)	(K)	(Cu)	(Rb)	(Ag)	(Cs)			(Au)		

**462.** In the two foregoing tables it would appear as if the elements might consist of six series (the odd-numbered series) of seven each, and six series (the even-numbered series) of ten each. Series 1, beginning with hydrogen, will probably be found to contain seven elements for the interval between the atomic weight of hydrogen and that of lithium is 6 and it will be seen that the intervals between the atomic weights of the members of the respective series immediately succeeding each other increase as the atomic weights become greater. Thus the difference between the atomic weights of Li and Na is 16, between those of Na and K also 16, between those of K and Cu 24.5, between those of Cu and Rb 22, between those of Rb and Ag 22.5, between those of Ag and Cs 25. Since the difference between the atomic weights of any two consecutive members of series 2 in no case exceeds 3 and averages only 2, while that difference in series 2 is only from 1 to 3.50, it would seem to be quite probable that undiscovered elements exist having atomic weights between 1 and 7 (H and Li) and between 19 and 23 (F and Na). It seems less probable that any elements exist having atomic weights between 35.4 and 39 (Cl and K), between 80 and 85.5 (Br and Rb), or between 126.5 and 133 (I and Cs).

Praseodymium, Neodymium, Gadolinium, Terbium, Erbium and Thulium all have atomic weights between those of Cerium (139) and Ytterbium (173).

While, reasoning from analogy, we should expect to find elements belonging to group VIII in series 2, it would seem less probable that any elements will be found belonging to group VIII in series 1.

But in the second table we find copper, silver and gold in the same group as the alkali metals; zinc, cadmium and mercury with the alkaline earth metals; lead in the same group with carbon; chromium, molybdenum, tungsten and uranium with oxygen and sulphur; and manganese among the halogens. These apparent anomalies are, however, by no means sufficient to disprove the assumption that the "periodic system" is based upon a real natural law.

**463.** Another table designed to show the periodicity of the recurrence of natural relationships between the elements is one that recognizes two "short periods" of seven elements each, and five "long periods" each containing seventeen elements:

Groups	Typical formulas of the higher saltforming oxides.	Short Periods.	Long or Large Periods.				
		Typical or 1st small Period.	1.	2.	3.	4.	5.
I.	$R_2O$	Li 7	K 39	Rb 85.5	Cs 133	.....	.....
II.	$RO$	Be 9	Ca 40	Sr 87.5	Ba 137.5	.....	.....
III.	$R_2O_3$	B 11	Sc 44	Y 89	La 138.5	Yb 173	.....
IV.	$RO_2$	C 12	Ti 48	Zr 90.5	Ce 139	.....	Th 232.5
V.	$R_2O_5$	N 14	V 51.5	Cb 98.5	.....	Ta 182.5	.....
VI.	$RO_3$	O 16	Cr 52	Mo 96	.....	W 184	U 238.5
VII.	$R_2O_7$	F 19	Mn 55	.....	.....	.....	.....
VIII.	{	2d small Period.	Fe 56	Ru 101.5	.....	Os 191	.....
			Co 59	Rh 103	.....	Ir 193	.....
			Ni 59	Pd 107	.....	Pt 195	.....
I.	$RO$	Na 23	Cu 63.5	Ag 108	.....	Au 197	.....
II.	$RO$	Mg 24	Zn 65.3	Cd 112	.....	Hg 200	.....
III.	$R_2O_3$	Al 27	Ga 70	In 114	.....	Tl 204	.....
IV.	$RO_2$	Si 28.4	Ge 72.5	Sn 119	.....	Pb 206.5	.....
V.	$R_2O_5$	P 31	As 75	Sb 120	.....	Bi 208	.....
VI.	$RO_3$	S 32	Se 79	Te 128	.....	.....	.....
VII.	$R_2O_7$	Cl 35.4	Br 80	I 126.5	.....	.....	.....

In this table it is seen that each "long period" may be regarded as consisting of two short periods of seven elements each, with triads of elements of group VIII in the middle, separating those short periods from each other.

This arrangement assumes that there are no elements having atomic weights between 19 and 23, and it does not provide any place for hydrogen. The separation of fluorine from the other halogens and of sodium from other alkali metals, and the grouping of decidedly metallic elements and decidedly non-metallic elements beside each other, are still the inevitable results, for which no satisfactory reasons are apparent. But the specific weights of the elements are lowest at the beginning and end of each period, being highest in the middle, and the atomic volumes\* progress in the opposite direction.

464. Another arrangement of the elements in natural groups according to their properties, and, at the same time, consistently with the order in which their atomic weights increase in each period, results as shown in the following table:

\*The atomic volume of an element is the number obtained by dividing the atomic weight by the specific weight of the element in the solid state.

Table of the Elements arranged according to their atomic weights and polarity-values.

+1	+2	+3	+4	+5	+6	+7		+1	+2	+3	+4	+5	+6	+7
Li 7. 12.	Be 9. 4.5							H 1.						
Na 23. 24.	Mg 24.2 14.	Al 27. 10.8												
K 39. 46.4	Ca 40. 25.4	Sc 44. 17.	Ti 48. 13.	V 51.5 9.8	Cr 52. 7.7	Mn 55. 6.9	Fe 56. 7.2	Cu 63.5 7.1	Zn 65.8 9.1	Ga 70. 11.7	Ge 72.5 13.2	As 75. 13.2	Se 79. 17.1	Br 80. 26.6
Rb 85.5 56.2	Sr 87.5 35.	Y 89. 24.7	Zr 90.5 22.6	Cb 98.5 18.3	Mo 96. 11.1		Ru 101.5 8.	Ag 108. 10.1	Cd 112. 12.8	In 114. 15.4	Su 119. 16.3	Sb 120. 18.	Te 126. 20.	I 126.5 25.3
Cs 133. 88.	Ba 137.5 34.3	La 138.5 21.	Ce 139. 21.											
		Yb 178. 26.		Ta 182.5 17.5	W 184. 9.7		Os 191. 8.6	Au 197. 10.	Hg 200. 14.7	Tl 204. 17.	Pb 206.5 18.	Bi 208. 20.		
			Th 232.5 21.		U 238.5 12.8									
+1	+2	+3	+4	+5	+6	+7		+1	+2	+3	+4	+5	+6	+7

Here it will be observed that the "two short periods" have been divided. Lithium and beryllium of Mendeleeff's first small period, and sodium, magnesium and aluminum of his second small period, have been placed to the left, while boron, carbon, nitrogen, oxygen and fluorine of the first and silicon, phosphorus, sulphur and chlorine of the second small period have been placed to the right. I have done this in the face of the fact that probably no elements having atomic weights between 9 and 11 and between 27 and 28.4 exist, for my object is to separate the clearly non-metallic elements from the clearly metallic elements, and to avoid the separation of lithium and sodium from the other alkali metals, beryllium from its near relative magnesium, carbon and silicon from their relatives germanium and tin, nitrogen and phosphorus from the closely related elements arsenic and antimony, sulphur from the other members of the same family, and the separation of fluorine and chlorine from the other halogens.

In this table, therefore, the elements are given a natural grouping still consistent with their arrangement according to their atomic masses and atomic volumes.

The atomic volumes, represented by the numbers placed below the atomic weights, are largest at the beginning and end of each (horizontal) period and smallest in the middle, as in Mendeleeff's table of long and short periods.

All of the elements in the first thirteen vertical columns or groups are elements which exhibit positive polarity in all their compounds, while all elements exhibiting positive polarity in some of their compounds and negative polarity in others are found in the upper two-thirds of the last four columns or groups.

The non-metallic elements are all to be found in the upper right hand corner of this table, while their antipodes are diagonally across the table in its lower left hand corner.

The maximum polarity-values (Chapter IX) of the respective groups are indicated at the top and bottom of the several columns, increasing regularly from +1 to +7 in the first seven groups, varying from +8 to +2 in the three middle columns (Mendeleeff's "Group VIII"), and again ranging regularly from +1 to +7 in the last seven groups but with the striking qualification that the negative polarity-value, exhibited first in the carbon group, decreases from -4 to -1 as regularly as the positive polarity-value increases, the difference between the units of maxi-

imum positive combining value and the negative combining value of each element in the four last groups being in every instance 8.

Carbon has a maximum polarity-value of  $+4$  in  $\text{CO}_2$ , and a lowest polarity-value of  $-4$  in  $\text{CH}_4$ ; nitrogen has a maximum polarity-value of  $+5$  in nitric acid, and a minimum polarity-value of  $-3$  in ammonia; sulphur has a maximum polarity-value of  $+6$  in sulphur trioxide, and a minimum polarity-value of  $-2$  in  $\text{H}_2\text{S}$ ; and chlorine has a maximum polarity-value of  $+7$  in perchlorates with a minimum polarity-value of  $-1$  in the chlorides.

Osmium and ruthenium, having a maximum positive valence of  $+8$ , are necessarily in the 8th group.

**465.** Among the striking facts connected with the "periodic law" may be mentioned the frequent occurrence of "triads" of closely related elements, of which one has an atomic weight almost exactly one-half of the sum of the atomic weights of the other two. Such triads are formed by: Ca, Ba and Sr; S, Se and Te; Cl, Br and I; P, As and Sb; F, Cl and Br; N, P and As; O, S and Se; Li, Na and K; K, Rb and Cs; etc. The differences between the atomic weights of elements belonging to the same group are frequently multiples of 8 or of 16. The differences are 16 or nearly so between the atomic weights of the following pairs: Li and Na; Na and K; Be and Mg; Mg and Ca; B and Al; Al and Sc; C and Si; N and P; O and S; F and Cl. In many other cases of two related elements the differences between their atomic weights are 24 or nearly so, or some other multiple of 8.

**466.** That the relative masses of the atoms furnish a fundamental indication of the properties of the elements and of the periodicity of the recurrence of analogies is now generally admitted.

The intensity of chemical energy increases as the atomic mass increases with elements whose polarity is positive and which perform basic functions; the intensity of the combining energy of elements exercising negative polarity decreases as the atomic mass increases. This tendency is most strikingly exemplified in the groups of the alkali metals and the alkaline earth metals, and in the halogen and oxygen groups.

Elements having a large atomic volume are relatively energetic, and *vice versa*. This may also be expressed by the statement: Chemical energy decreases as density rises, and *vice versa*. Thus the alkali metals and the halogens have greater intensity of chemi-

cal energy than intermediate groups because they have a less density or a greater atomic volume.

That the alkali metals and the halogens are chemical opposites is evident from the fact that when an alkali metal decomposes water it is the hydrogen of the water which is liberated; but when a halogen decomposes water it is the oxygen which is set free. The alkali metal enters into combination with the oxygen, but the halogen with the hydrogen of the compound formed by hydrogen and oxygen with each other.

The sixteen elements in the last four columns in the upper right hand corner of the table are the only elements capable of combining directly with hydrogen\*, and these elements never perform basic functions in the formation of salts.

The only element having no known oxygen compound is fluorine which stands next after oxygen and just above chlorine, and the only two elements which invariably exercise negative polarity in all their compounds are fluorine and oxygen.

The elements embraced in the first two groups, the alkali metals and alkaline-earth metals, never perform acidic functions.

Not any two of the elements placed in the first thirteen vertical columns combine directly with each other.

In each group containing elements which form chemical compounds with each other any element having a greater atomic mass is relatively positive toward any element (of the same group) having a smaller atomic mass. Thus we can not have an iodide of bromine, chlorine or iodine, nor a bromide of chlorine or fluorine; but we do have chlorides of bromine and iodine, and bromides of iodine.

So far as they enter into direct combination with each other all elements to the left are relatively of positive polarity toward elements to the right in this table.

But of the non-metallic elements, *when exercising negative polarity*, any element having a lower atomic mass generally exhibits a more powerful or intense chemical energy than one of greater atomic mass.

Cæsium is the most powerful positive element, and fluorine the most powerful negative element.

\*Potassium, sodium and palladium are said to combine with hydrogen; but these so-called compounds are altogether metallic in their properties and in all probability only alloys, which do not resemble true chemical compounds any more than solutions do.

The strongest acids are the hydroxyl acids of nitrogen, sulphur and phosphorous and the hydrogen acids of chlorine and bromine.

Elements having atomic weights exceeding 150 as a rule exercise rather feeble basic functions.

**467.** The principal elements entering into the compounds of organic chemistry are carbon, hydrogen, oxygen and nitrogen—only four. But these four elements, and, indeed, three of them, are capable of forming innumerable kinds of molecules. This may be understood when it is remembered that these elements have not only different valences but the greatest possible range of polarity-values.

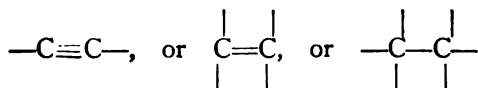
Hydrogen is invariably of positive polarity and a monad.

Oxygen is invariably of negative polarity and a dyad.

Nitrogen may be either a monad or a dyad, triad, tetrad, or pentad, and it may be either positive or negative, or it may have both positive and negative bonds so that its polarity-value (or the algebraic sum of its units of combining value) may be  $-3$  or  $+1$ ,  $+2$ ,  $+3$ ,  $+4$ , or  $+5$ . The nitrogen atom may be a negative triad, or it may be a pentad with the same polarity-value ( $-3$ ).

Carbon is in all organic compounds a tetrad, but its polarity-value may be either  $-4$ , or  $-2$ , or  $0$ , or  $+2$ , or  $+4$ .

While hydrogen, being a monad, is for that reason incapable of performing a linking function, the other three elements are not only able to link together two or more atoms of one or more other elements, but two or more of the atoms of one of them may be united to each other in the structure of compound molecules. Carbon especially exhibits a wonderful power to form chains. Any two carbon atoms, each having four bonds, may be united to each other in three different ways:



The remaining bonds of these groups may assume either positive or negative polarity according to the nature of the elements with which the carbon may be united. Finally we find that three or more carbon atoms may form chains, clusters, and rings which still present remaining bonds to which other atoms, chains, clus-

ters and rings are linked. Manifold groups, rings and branching chains, or combinations of these may be formed.

Sulphur, standing close to oxygen, is also found to be a constituent element in important organic substances. Sulphur, when it exercises exclusively negative polarity, is a dyad and capable of performing a linking function in the same manner as oxygen, which it can replace without changing the general plan of the structure of the molecule. The range of the respective polarity-values of a sulphur atom in combination includes  $-2$ ,  $0$ ,  $+2$ ,  $+4$  and  $+6$ , and we sometimes find both positive and negative sulphur together, and directly united to each other, in one and the same molecule, the positive sulphur performing radically different functions from those performed by the negative sulphur.

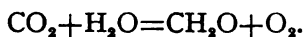
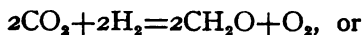
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The degree of obedience of the highly organized bodies of man, animals and plants to the causative and determining power of the life which animates them must depend upon the variety, plasticity and adaptability of the molecules which are acted upon and which react in response to the impulse. The elements composing organic substances have small atomic weights and low specific weights; compounds of elements having high atomic and specific weights seem rather to cause obstruction or disturbance of the normal functions of the delicately adjusted systems of organized bodies.

As a rule the most complex molecules are very sensitive and most obedient to the commands of energy. It is significant that these most complex molecules are found only in living organisms, and that they break up into simpler molecules when life ceases to act upon or rather through them. The formation of such marvelous molecular structures as those of the substances which serve for the embodiment of plants, animals and man is impossible except through the influence (inflowing) of life itself, which is capable of infinite variety of manifestation. The chemist can not cause the elements carbon, hydrogen and oxygen to combine with each other to form the substances necessary to the nourishment of plants and animals. But the plants appear to be the instruments employed to construct and arrange the molecules required for their own use and for the higher uses of animals and man.

Earth, air and water furnish the materials. Chief among these are water and air. Carbon dioxide is taken up from the air and

in place of one of its oxygen atoms. Life inserts, through the agency of the plant, two hydrogen atoms taken from water :



The comparatively simple molecule of formaldehyde,  $\text{CH}_2\text{O}$ , is believed to be transformed by condensation into  $\text{C}_6\text{H}_{12}\text{O}_6$ , which furnishes cellulose, starch, sugar, etc.

The architecture of the house of each species of plant or animal possesses a striking individuality in the most minute particulars no less than in the general outlines of the exterior. The instances of "artificial" production in the laboratory of certain molecules before supposed to be not creatable outside of living bodies are so rare and of such a character as to indicate unmistakably that physical and chemical energy are not alone sufficient to account for life processes and their products, however skilfully man may discover and prepare the right conditions requisite to definite results of the operation of natural laws in other directions.

Although the same elements enter into the formation of the molecules of all quaternary alkaloids, the quality of the life of the *Cinchona* directs and determines the movements of the atoms toward the construction of molecules of quinine but not morphine, while the quality of the life of *Papaver somniferum* builds morphine but not quinine. The particular kind of bark which clothes the trunk of the birch is possible only to the birch. The oak is in the acorn laying the foundation for its house which it finishes long after the acorn has disappeared. No living being builds just such a house except the oak; and it is for this reason that most men mistake the house for the oak itself.

The birch makes one kind of bark; the oak another. But both may grow side by side in the same soil. The oyster and the clam build very different shells; but both use precisely the same materials.

The extremely complex molecules of oxyhæmoglobin and other substances necessary to the human body can not be constructed except *in* that body, but not *by* it or by any of its parts; they can be formed only through the mediation of its living inhabitant, for they are not formed in or by the cadaver.

## CHAPTER XXVII.

### A RECAPITULATION OF FUNDAMENTAL FACTS, DEFINITIONS AND HYPOTHESES.

**468. Matter** is that which occupies space, and is affected by gravitation and capable of motion.

**469.** All matter is made up of minute indivisible particles called **atoms**.

**470.** As atoms are indivisible and therefore undecomposable, and as all matter is made up of atoms, all the distinct kinds of atoms are called the **elements** of matter or chemical elements.

**471.** The number of distinct kinds of atoms is limited and constant. About eighty kinds are now known.

**472.** All atoms of any one kind have the same mass and, in all respects, the same properties.

**473. Molecules** are the smallest distinct individual particles of matter capable of independent existence. They may consist of one or more atoms.

**474. Chemistry** is the science of the composition, structure and relative stability of molecules.

**475. Chemism** is the attraction by which atoms are united in chemical combination.

**476.** Chemism is one of the several distinct forms of energy. But it is atomic energy, whereas all other forms of energy are either molecular or molar.

**477.** The number of distinct kinds of molecules is countless.

All molecules of any one kind have the same mass and, in all respects, the same structure and properties.

**478.** Molecules consisting of but one atom, and molecules consisting of two or more atoms of but one kind, are **elemental molecules**.

**479.** Molecules consisting of two or more different elements are compound molecules or **chemical compounds**.

**480.** The identity of any substance or distinct kind of matter is the identity of its molecule.

**481.** A true chemical compound consists of but one kind of molecules.

**482.** Chemism is like a polar force, and atomic attraction is dependent upon the relatively opposite polarities of the atoms which mutually attract each other.

**483.** **Chemical polarity** is the quality of the chemism of an atom in actual combination.

**484.** No two atoms can be held in combination with each other unless they have opposite chemical polarities.

**485.** The chemical polarity of hydrogen in combination with any other element is always positive, and the polarity of any atom in direct combination with hydrogen is, therefore, and to that extent, always negative.

**486.** The chemical polarity of oxygen in combination with any other element is always negative, and the polarity of any atom in direct combination with oxygen is, therefore, and to that extent, always positive.

**487.** **Valence** is the measure of the relative capacity of a definite number of individual atoms of one kind to hold in combination a definite number of atoms of a different kind.

**488.** Atomic valence is limited. No one atom of any kind can hold in combination with itself more than six atoms of any one other kind.

The highest valence attained by any atom is eight times as great as the lowest valence attained by any atom.

**489.** The valence of any atom of negative chemical polarity is expressed by the number of hydrogen atoms which it holds in combination directly with itself.

**490.** The valence of any atom of positive chemical polarity is expressed by one-half of the number of oxygen atoms which it holds in combination directly with itself.

**491.** Any given atom has the same valence in every compound in which it exercises exclusively negative polarity.

**492.** Variable atomic valence is possible to elements in the exercise of positive polarity.

**493.** A free atom has neither polarity nor valence; but any free atom has the capacity to acquire both polarity and valence, which are excited in it by the atom or atoms with which it enters into combination.

**494.** All atoms in chemical combination have polarity and valence.

**495.** The polarity and valence of any combined atom are de-

terminated primarily by the atom or atoms with which it is in direct combination.

**496.** Hydrogen, because it becomes itself positive, excites negative polarity in any other element with which it enters into direct chemical combination.

**497.** Oxygen, because it becomes itself negative, excites positive polarity in any other element with which it enters into direct chemical combination.

**498.** The units of valence of any atom in chemical combination are called **bonds**.

**499.** The units of valence by which any atom is united to any element of positive polarity are called **negative bonds**; and the units of valence by which any atom is united to any element of negative polarity are called **positive bonds**.

**500.** To distinguish between positive and negative units of atomic combining value, the positive units (or the positive bonds) are designated as plus quantities (indicated by the *plus* sign), and the negative units (or the negative bonds) are designated as minus quantities (indicated by the *minus* sign).

**501.** The *true combining value* of any atom in combination is not its valence; it can be expressed only in terms referring to both polarity and valence.

**502.** The **polarity-value** of any atom in combination is the algebraic sum of its positive and negative bonds, and the true combining value of any atom is its polarity-value.

**503.** The arithmetical sum of the bonds of any atom without reference to chemical polarity expresses its valence; but the algebraic sum of the positive and negative bonds of any atom, expressing its actual combining value, must be either a plus quantity or a minus quantity, or zero.

**504.** That the polarity-value of an atom is its real combining value, and not merely an arbitrary expression employed to distinguish between positive and negative bonds, is conclusively demonstrated by the following proofs:

*a.* There is no difference between the *valence* of an atom having 4 *positive* bonds and that of an atom having 4 *negative* bonds; but the difference between their respective *polarity-values* amounts to 8 units, for it is the difference between +4 and -4. To change 4 positive bonds into 4 negative bonds actually con-

sumes just 8 units of reducing power by whatever reducing agent the change may be effected.

To change any positive tetrad into a negative tetrad, or a positive pentad into a negative triad, or a positive hexad into a negative dyad, or a positive heptad into a negative monad—any one of these changes consumes 8 units of reducing power.

*b.* One molecule of  $\text{KMnO}_4$  acting as an oxidizing agent (in the presence of sulphuric or hydrochloric acid) invariably exercises an oxidizing power the exact measure of which is 5 units, because the Mn in  $\text{KMnO}_4$  has a polarity-value of  $+7$ , whereas in the manganous salt formed by the reduction of the permanganate the Mn has a polarity-value of  $+2$ . This shows why it is that just two molecules of  $\text{KMnO}_4$  are required to change five uncombined atoms (having a polarity-value of zero) into five positive dyads, or to change five positive dyad atoms into five positive tetrad atoms, or five positive tetrads into five positive hexads. To change five negative triad atoms into five positive pentads consumes all of the oxidizing power of 8 molecules of  $\text{KMnO}_4$ .

*c.* Each molecule of hydrogen (two combined atoms) when used as a reducing agent lowers the polarity-value of the element reduced by it to the extent of two units, for the molecule of hydrogen contains one atom of H with a polarity-value of  $+1$  and one other atom of H with a combining value of  $-1$ ; it is the latter atom which acts as a reducing agent for it acquires, by the reaction, a polarity-value of  $+1$ , and this change from a polarity-value of  $-1$  to one of  $+1$  is a change of two units and requires two units of oxidizing power.

A free atom of hydrogen (nascent hydrogen) has a polarity-value expressed by 0, and when it acts as a reducing agent it acquires a polarity-value of  $+1$ .

Hence for each atom of hydrogen used as a reducing agent 1 unit of polarity-value is taken from the atom reduced. Accordingly all of the reducing power of 8 atoms of hydrogen (free, or combined into four molecules of  $\text{H}_2$ ) is consumed in changing any positive pentad atom into a negative triad, or four positive hexad atoms into four positive tetrad atoms, or one positive hexad atom into a negative dyad, or one positive tetrad into one negative tetrad; or to liberate 8 positive monads, or 4 positive dyads, or 2 positive tetrads, from combination.

*d.* The nitrogen atom in the molecule  $\text{H}_3\text{N}$  has three negative

bonds and hence a polarity-value of  $-3$ . In the molecule  $\text{H}_4\text{NNO}_3$  the first nitrogen atom has a polarity-value of  $-3$ , and the second a polarity-value of  $+5$ ; but each nitrogen atom here has 5 bonds. The first nitrogen atom has 4 negative and 1 positive bond; the other has 5 positive bonds.

Whenever ammonia, or an amine, or pyridine, or quinoline, or any alkaloid, combines with any acid to form a halide or a salt, the negative nitrogen acquires 2 new bonds, *but it is neither oxidized nor reduced*, for its polarity-value still remains  $-3$ . One of the new bonds acquired by the nitrogen atom is *positive* and links it to the halogen or oxygen; the other new bond is *negative* and links the N to the hydrogen of the acid.

**505.** No atom attains a lower valence than 1; but its lowest polarity-value may be  $-4$ .

**506.** No atom attains a higher valence than 8; nor a higher polarity-value than  $+8$ .

**507.** The difference between the highest polarity-value attainable by any atom of any particular kind and the lowest polarity-value attainable by *the same atom* in no case exceeds 8 units.

**508.** The difference between the highest polarity-value attainable by any atom and the lowest polarity-value attainable by any atom amounts to 12 units.

**509.** A free atom has no bonds; it acquires bonds whenever it enters into combination with any other atom or atoms.

**510.** An atom in combination always has bonds; it loses these bonds whenever it is completely released from combination.

**511.** The sum of the units of atomic *valence* of matter is variable, for an atom may acquire additional bonds without taking those additional bonds from any other atom.

(This happens as the nitrogen of ammonia changes from a triad to a pentad, when the ammonia forms a halide with a hydrogen acid, or a salt with a hydroxyl acid.)

**512.** The algebraic sum of the units of polarity-value of all atoms of all matter is always zero.

**513.** There can be no increase or diminution in the polarity-value of any atom or atoms without a concurrent and exactly corresponding diminution or increase in the polarity-value of some other atom or atoms.

**514.** **Oxidation** is an increase of polarity-value.

**515.** **Reduction** is a diminution of polarity-value.

**516.** Oxidation and reduction are measured in units of polarity-value.

A unit of polarity-value gained is a **unit of oxidation**.

A unit of polarity-value lost is a **unit of reduction**.

**517.** An atom in combination may gain additional bonds by oxidation; or it may lose bonds by suffering reduction; or it may acquire an even number of additional bonds (one-half of them positive and the other half negative) without oxidation; or it may drop an even number of bonds without reduction.

**518.** The bonds of any atom having more than one bond may be either positive or negative, or a part of them positive and the remainder negative.

(Of the non-metallic elements only hydrogen and boron are invariably of positive polarity in all their compounds; oxygen and fluorine are the only two elements which are invariably negative in all their compounds; carbon, silicon, nitrogen, phosphorus, arsenic, sulphur, chlorine, bromine and iodine are positive in some compounds, but negative in others; and atoms of carbon, nitrogen and phosphorus may have both positive and negative bonds concurrently.)

**519.** Any two atoms directly combined with each other are united by an equal number of bonds of each atom, and, as the chemical polarity of the bonds of one of the atoms must be the opposite of the polarity of the bonds of the other, it follows that the algebraic sum of the positive and negative bonds by which any two atoms are held in combination in any molecule must be zero, and that the algebraic sum of all of the positive and negative atomic bonds in any molecule, whether elemental or compound, diatomic or polyatomic, must be zero.

**520.** When two or more atoms of one element are contained in one compound molecule, one or more of the atoms of that element may exercise positive polarity while the remaining atom or atoms may be of negative polarity; or a part of the atoms may be of one polarity and the remainder of divided polarity; or, if more than two atoms of the same kind are present, a part may be positive, a part negative, and the remainder of divided polarity.

**521.** In all compounds of carbon, hydrogen and oxygen the carbon bonds united to hydrogen are of negative polarity, and the carbon bonds united to oxygen are of positive polarity; but the bonds by which any two or more carbon atoms are united

directly to each other are one-half of them positive and the other half negative.

**522.** Since each carbon atom in any compound containing more than one such atom has four bonds; and since the algebraic sum of all the positive and negative bonds in any molecule must be zero, it follows that the number of carbon atoms united directly to each other in any molecule composed of carbon, hydrogen and oxygen, and the exact number of bonds by which they are thus united to each other in any such molecule, can be readily found from its molecular formula.

**523.** Any atom sustaining a diminution of polarity-value is an **oxidizing agent**.

**524.** Any atom gaining an increase of polarity-value is a **reducing agent**.

**525.** Any free hydrogen atom whenever it enters into combination with any atom of another kind acts as a reducing agent because it thereby acquires one positive bond.

**526.** Any free oxygen atom whenever it enters into combination with any atom or atoms of one or more other elements acts as an oxidizing agent because it thereby acquires two negative bonds.

**527.** A molecule of hydrogen contains one atom having a positive bond and one atom having a negative bond. Whenever it reacts with any other kind of matter its positive atom suffers neither oxidation nor reduction, but its negative atom *gains two* units of polarity-value without gaining or losing any unit of valence; the negative atom of the hydrogen molecule, when it becomes linked to any other element, has its polarity-value changed from  $-1$  to  $+1$ ,—a difference of two units.

(Negative hydrogen atoms exist only in the molecules of hydrogen.)

**528.** A molecule of oxygen contains one atom having two positive bonds and one atom having two negative bonds. Whenever it reacts with any other element its negative atom suffers neither oxidation nor reduction, but its positive atom *loses four* units of polarity-value without gaining or losing any unit of valence; the positive atom of the oxygen molecule, when it becomes linked to any other element, has its polarity-value changed from  $+2$  to  $-2$ ,—a difference of four units.

(Positive oxygen atoms exist only in the molecules of oxygen.)

**529.** Whenever two free hydrogen atoms unite with each other to form a molecule of hydrogen, one of the atoms acquires one positive bond and the other one negative bond. In other words, one of the atoms is oxidized and the other reduced.

**530.** Whenever two free atoms of oxygen unite with each other to form a molecule of oxygen, one of the atoms acquires two positive bonds and the other two negative bonds. In other words, one atom is oxidized and the other reduced.

(It may be, however, that each oxygen atom acquires one positive and one negative bond, the positive bond of each being linked to the negative bond of the other, as represented by  $O \overset{+}{-} \overset{-}{+} O$ .)

**531.** Whenever a molecule of hydrogen is split up into two free hydrogen atoms, both atoms lose their bonds; one atom is oxidized and the other reduced.

**532.** Whenever a molecule of oxygen is split up into two free oxygen atoms, both atoms lose their bonds; one atom is oxidized and the other reduced.

**533.** All oxidizing agents and reducing agents are atoms. They may be free atoms, or atoms contained in elemental molecules, or atoms contained in compound molecules.

**534.** The oxidizing and reducing agents in any one reaction may be atoms of the same kind or atoms of different kinds; they may both be contained in the same molecule, or in separate molecules; and, if contained in separate molecules, these molecules may be of the same kind or of different kinds.

**535.** The relative positions of the atoms contained in any molecule are determined by the respective polarities and valences of the component atoms, and are invariably the same in every respect in all molecules of any one kind.

**536.** The manner in which the component atoms of any molecule are held together in definite relative positions according to their respective polarities and units of valence, is called the **atomic linking** of that molecule.

**537.** The atomic linking of any molecule consisting of two or more atoms is unbroken, so that all of the atoms of any molecule are held together into one united system.

**538.** A **true chemical compound** is a group of two or more different kinds of atoms held together by atomic attraction and forming one unbroken system of atomic linking.

**539.** Substances of definite composition having more than one

system of atomic linking are not true chemical compounds, for they do not result from atomic attraction in accordance with the laws of polarity and valence. Such substances are made up of as many independent molecules as the number of their independent systems of atomic linking. They are, therefore, **molecular combinations**, or aggregations resulting from some form of molecular attraction.

(Examples of substances of definite composition, but which nevertheless have two or more independent systems of atomic linking, are furnished by crystallized substances containing water of crystallization and other substances holding definite proportions of water.)

If this be not admitted, then the theory of valence must be rejected, for all that is at present known concerning the structure of molecules is founded upon their probable atomic linking, which is discoverable only by the aid of the hypotheses of chemical polarity and atomic valence.

**540. A true chemical change is a change of atomic linking.**

**541.** The atomic linking of the molecules of inorganic compounds is generally very simple and readily traced.

The atomic linking of complex molecules is not easily discovered, and it is rarely discoverable without the aid of various analytical and synthetical reactions and other facts, relationships and properties of the substances concerned. But in no case can a structural formula be satisfactorily or intelligibly represented without the aid of the hypotheses of chemical polarity and atomic valence.

**542.** Any assumed structural molecular formula which violates the hypotheses of chemical polarity and atomic valence can not be the true formula.

**543.** By the aid of the conception of polarity-value we are enabled to see clearly that there can be no such chemical compound as a pentasulphide of calcium,  $\text{CaS}_5$ . In order to be a sulphide all of its sulphur atoms must be of negative polarity and have the invariable polarity-value of  $-2$ ; this would require us to assign to the calcium atom a polarity-value of  $+10$ , which it can not have since no atom of any kind ever assumes a polarity-value exceeding  $+8$ . If, on the other hand, we assign to the calcium atom its true polarity-value of  $+2$ , then each sulphur atom would have a valence of  $\frac{2}{5}$ , which would be an equally

absurd proposition. We are, therefore, obliged to conclude that *CaS<sub>5</sub> is not a sulphide*. As the Ca unquestionably has a polarity-value of +2 the *algebraic sum* of the bonds of the five sulphur atoms *must* be -2, and this leads to the final decision that one of the sulphur atoms has the polarity-value +6 and performs the acidic function, while each of the other four sulphur atoms has a polarity-value of -2, so that the compound is calcium tetrathiosulphate, CaSS<sub>4</sub>, corresponding to CaSO<sub>4</sub>, which is rational and consistent and confirmed by the fact that only a portion of the sulphur of the CaSS<sub>4</sub> (empirically written CaS<sub>5</sub>) can be precipitated as CuS with a solution by Cu (NO<sub>3</sub>)<sub>2</sub>.

The recognition of the hypothesis that the polarity-value of an atom is the true measure of its combining value at once enables us to see that a potassium sulphide having the formula K<sub>2</sub>S<sub>3</sub> can not exist, and that the compound so represented is in reality K<sub>2</sub>SS<sub>2</sub> corresponding to K<sub>2</sub>SO<sub>2</sub>. It also enables us to see that sodium thiosulphate is not Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, but Na<sub>2</sub>SO<sub>3</sub>S, and that hypophosphorous acid is not H<sub>3</sub>PO<sub>2</sub>, but HPO<sub>2</sub>H<sub>2</sub> or HPH<sub>2</sub>O<sub>2</sub>, in which the phosphorus atom has a *valence* of 5 but a polarity-value of +1. We know experimentally that to oxidize hypophosphites to phosphates (in which the P has a polarity-value of +5 which is four units higher than +1) consumes just 4 oxidation units whatever the oxidizing agent may be.)

**544.** The chemical tendency of all matter is toward the formation of molecules of the greatest **stability** under the conditions to which it is, at the time, subject.

When these conditions change to such an extent that the equilibrium between the various forces which directly or indirectly aid or oppose atomic attraction is overstepped, a rearrangement of the atoms into new molecules (which are stable under the new conditions) takes place.

**545.** The universal predisposition toward the formation of simple, stable molecules, in which the "selective" and "saturating" "affinities" and the ruling valences of the component radicals are as fully satisfied as the composition of the reacting molecules admits, frequently predetermines the concurrent formation of complex and relatively unstable molecules of unusual structure, and such complex and unusual molecular structures are probably always the results of oxidation and reduction under the dominating influence of predisposing affinities. Thus the uni-

versal tendency toward a stable chemical equilibrium often predetermines the formation of the most powerful radicals of opposite polarity which can be formed out of the reacting atomic groups in order that these opposite radicals may unite to form relatively stable compounds. The presence of a strong base often predetermines the formation of an acid with which that base can form a salt, and the presence of a strong acid predetermines the formation of a salt of that acid by causing one of the elements of one of the reagents to assume a valence consistent with basic functions. The valence of the manganese atom in  $\text{MnO}_2$  is not that of either basic manganese or acidic manganese, but  $\text{KOH}$  causes the  $\text{Mn}$  to assume acidic functions and the higher valence consistent therewith, whereas  $\text{H}_2\text{SO}_4$  causes it to assume basic functions and a lower valence.

**546.** An element forming one or more bases performs a **basic function**.

Metals perform the basic function in metallic salts.

**547.** An element forming one or more hydroxyl acids performs the **acidic function**.

The element linked by oxygen to the basic metal in a metallic salt is the acidic element of that salt.

**548.** The simple metallic oxygen-salts of the inorganic acids are composed of three kinds of atoms. These are: 1, the oxygen; 2, the atom or atoms of the metal performing the basic function; and 3, the atom or atoms of the element performing the acidic function (usually a non-metallic element).

**549.** Three different elements are necessary to the formation of any inorganic base (a metallic hydroxide having basic properties), namely: 1, the basic element (a metal); 2, oxygen; and (3) hydrogen.

**550.** Three different elements are necessary to the formation of any inorganic hydroxyl acid, namely: (1) the acidic element (2) oxygen, and (3) hydrogen.

**551.** Since oxygen and hydrogen are the constant elements common to both acids and bases it is evident that the acid nature of the acids can not be due to either the oxygen, or the hydrogen, or the hydroxyl, but is due to the element performing the acidic function (the acidic element); and the alkaline character of the soluble bases can not be due to either the oxygen or the hydrogen,

or the hydroxyl, but is due to the element performing the basic function (the basic element).

**552.** Elements capable of combining directly with hydrogen never perform basic functions.

**553.** The metals generally have the power to perform the basic function in the formation of bases and salts.

Some of the metals also have the power to perform the acidic function.

Whenever any metal possesses the capacity to exercise basic functions in some of its compounds and acidic functions in others, it commonly exhibits a higher (but never a lower) polarity-value as an acidic element than it does as a basic element.

**554.** The element performing the acidic function and the element performing the basic function in the formation of any oxygen salt must both exercise positive chemical polarity, both being linked immediately to oxygen.

Acidic functions and basic functions are opposite in the sense that acids and bases neutralize each other; but the chemical polarity of any atom or unsaturated group of atoms (compound radical) is determined by the atom or atoms to which it is or becomes immediately linked.

**555.** Elements capable of performing basic functions but unable to perform acidic functions are never found directly linked to each other *in true chemical compounds*; but such elements do generally unite directly with elements capable of performing acidic functions but unable to perform basic functions.

**556.** The strongest acids, forming the most stable salts and capable of decomposing the salts of other acids, are generally acids in which the acidic element exercises a high polarity-value.

**557.** The strongest bases, forming the most stable salts and capable of decomposing the salts of other bases, are generally those in which the basic element exercises a low polarity-value.

**558.** The four halogens are all negative monads; that is, their chemical polarity is invariably negative and their polarity-value —1. Whenever their polarity-value changes (increases) they cease to be halogens, their chemical polarity is reversed, and they assume the rôle of acidic elements.

**559.** The several different correct structural formulas consistent with any empiric formula are all consistent also with the conception of polarity-value.

**560.** A correct conception of polarity-value renders the reducing action of  $\text{H}_2\text{O}_2$  in respect to  $\text{KMnO}_4$  intelligible; it shows that the decomposition of  $\text{H}_2\text{O}_2$  into  $\text{H}_2\text{O}$  and  $\text{O}$  involves neither oxidation nor reduction; and enables us to balance in a rational way all chemical equations in which oxidation and reduction take place.

**561.** The oxygen of the atmosphere is the primary and inexhaustible oxidizing agent from which all other oxidizing agents, either directly or indirectly, derive their oxidizing power.

**562.** Of any two elements belonging to the same family but nevertheless capable of combining directly with each other, the one having the higher atomic weight is the positive element and the other the negative element in any compound they may form together; and if their respective atomic valences differ, then the element having the higher atomic weight also has the higher valence.

**563.** Of several elements belonging to one family and all exercising *positive* polarity, the one having the *highest* atomic weight generally exhibits the greatest intensity of chemical energy; but when their polarity is *negative* the element having the *lowest* atomic weight exhibits the greatest energy.

**564.** Of any series of elements arranged consecutively in the order of their increasing atomic weights, the elements having the lowest valences usually exhibit the greatest chemical energy.

**565.** Gaseous elements combine in simple volume-proportions, and the volumes of the products bear simple relations to the volumes of the factors.

**566.** Equal volumes of all gases contain the same number of molecules.

Hence it follows that the molecular weight of any given kind of molecules is expressed by twice the number expressing its vapor-density.

**567.** The number of atoms contained in any molecule is found by dividing its molecular heat by 6.4. (See Chapter V.)

Matter occurs: 1, in single free atoms or monatomic molecules; 2, in elemental molecules of two or more atoms; 3, in compound molecules having an unbroken system of interatomic linking consistent with the theory of valence; 4, in atomic groups consisting of a definite number of atoms held together in a manner not consistent with the theory of atomic linking or valence, but nevertheless generally recognized as molecules in conformity to the law of the relation of molecular weight to vapor density; 5, homogeneous substances of definite composition but evidently containing more than one kind of molecules; 6, homogeneous substances of indefinite composition evidently containing more than one kind of molecules; 7, substances not homogeneous.

One or more of the recently discovered gaseous elements contained in the atmosphere are believed to consist of free atoms or monatomic molecules even at ordinary temperatures.

Several elements which are not gaseous at ordinary temperatures apparently consist of free atoms or monatomic molecules when in a state of vapor, as, for instance, mercury, zinc and cadmium.

Several elements which at certain temperatures, while in a state of vapor, have diatomic molecules apparently consist of monatomic molecules at higher temperatures, as, for instance, chlorine and iodine.

Some elements having diatomic molecules at very high temperatures seem to have polyatomic molecules at lower temperatures, as, for instance, sulphur.

True compound molecules always have a definite and unbroken system of atomic linking in accordance with the theory of valence, as, for instance,  $\text{AlCl}_3$ ,  $\text{FeCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{KCl}$ .

Such atomic groups as  $\text{Al}_2\text{Cl}_6$ ,  $\text{Fe}_2\text{Cl}_4$  and  $\text{Fe}_2\text{Cl}_6$  are recognized as molecules in conformity to the law of the relation of molecular weight to vapor density; but their structure is inconsistent with the theory of valence.

Substances such as  $\text{FeCl}_2 \cdot 2\text{KCl}$ ,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , are of definite composition but clearly consist of more than one kind of molecules, each kind having its own independent system of atomic linking.

Solutions and alloys are apparently homogeneous but are not of definite composition, and certain substances in water-solution

are regarded as existing in a state of partial dissociation into free ions.

The molecules of chemically homogeneous substances (containing but one kind of molecules), as the metals, water, bromine, alcohol, anhydrous salts and halides, are held together more or less firmly by cohesion.

Many pairs of chemically homogeneous substances are intimately blended into solutions, alloys, etc., by that form of molecular attraction which is called adhesion.

Mixtures of various kinds of matter may be held together by adhesion, while others are apparently not affected by any form of molecular attraction.

Finally, all matter is subject to that universal form of attraction called gravitation.

**PART II.**

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**ELEMENTARY**

**DESCRIPTIVE CHEMISTRY.**



# ELEMENTARY DESCRIPTIVE CHEMISTRY

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## CHAPTER XXVIII.

### ORDER OF STUDY OF THE ELEMENTS AND THEIR COMPOUNDS.

**568.** The "periodic system" (Chapter XXVI) of classification of the elements will not be closely followed in the discussion of individual elements and their properties and compounds.

Hydrogen and oxygen will be first described because of their striking individuality and importance. Both are the ever-present constituents of all hydroxyl acids and bases as well as the component elements of water. All other elements may be advantageously classified into two groups according to their behavior toward hydrogen: 1, Elements that unite directly with hydrogen; and 2, elements that do not unite directly with hydrogen. This classification at once separates the elements into those that may from a strictly chemical standpoint be called non-metals, and those that are chemically metallic elements. It is also practicable and instructive to divide the elements into: 1, Those that unite directly with hydrogen and do not exhibit metallic luster, hardness and density (the non-metallic elements); 2, those that unite directly with hydrogen but possess metallic luster, hardness and density (arsenic and antimony); and 3, those that do not unite directly with hydrogen.

Elements not uniting directly with hydrogen do not perform basic functions, but all of them, except oxygen and fluorine, perform the acidic function in the formation of acidic hydroxides.

Hydrogen invariably exercises positive polarity in all its compounds and all elements not capable of directly combining with hydrogen are also of invariably positive polarity.

For these several reasons hydrogen will be described first.

Oxygen is the second element entering into the composition of water, and is contained in all oxides, hydroxides, and oxygen salts.

All elements except fluorine form binary compounds with oxygen.

Oxygen is the most abundant element in the world, exists in the free state in the air, and constitutes the exhaustless primary oxidizing agent capable of imparting actual and additional combining value to other elements.

Oxygen invariably exercises negative polarity in all its compounds.

For the reasons just stated we shall describe oxygen next after hydrogen.

All other elements are of negative polarity toward hydrogen and of positive polarity toward oxygen.

The polarity-value of combined hydrogen is invariably  $+1$ , and that of combined oxygen is invariably  $-2$ .

Water, the hydroxide of hydrogen (or its "oxide"), is the most important of all chemical compounds in the economy of Nature, in chemical operations, and in its relations to the most important classes of compound molecules.

**569.** Next in importance after hydrogen and oxygen are the elements of the chlorine family.

They exhibit great intensity of chemical energy and form binary compounds with all other elements, except that fluorine does not combine with oxygen.

Fluorine, chlorine, bromine and iodine invariably exhibit a polarity-value of  $-1$  in all of their compounds with other elements except when they unite directly with oxygen. When one of these elements having a higher atomic weight unites with another element of the same family having a lower atomic weight the element of the higher atomic weight is of positive polarity and frequently of higher valence.

The binary compounds formed by the negative non-metallic monads (the halogens) are necessarily of simple structure.

When chlorine or iodine is directly united to oxygen the chlorine or iodine exercises a polarity-value of  $+7$  or  $+5$  or  $+3$  or  $+1$ , and bromine in direct combination with oxygen exercises a polarity-value of  $+5$  or  $+3$  or  $+1$ .

**570.** Sulphur will be studied next on account of the great importance of the close analogy between oxygen and negative sulphur; because sulphur combines directly with all other ele-

ments; and because of the importance of the acids formed by that element.

Selenium and tellurium closely resemble sulphur in their chemical traits.

**571.** The negative monads and dyads are the *salt-forming elements*, for they are, one or the other, necessary to the formation of all salts.

The negative monads or halogens form the salts called *halides*; oxygen is a necessary constituent of all ordinary salts, called *true salts* or oxygen salts; and sulphur is the constant constituent of the class of salts called *sulphur salts*.

Selenium and Tellurium form salts analogous to the sulphur salts.

A comparative exhibit of the two classes of salt-formers, showing the parallelism of their atomic weights, is striking:

TRUE SALT FORMERS.	DYADS.	MONADS. HALOGENS.	
	<i>Atomic weights.</i>	<i>Atomic weights.</i>	
Oxygen .....	16	19	Fluorine
Sulphur .....	32	35.4	Chlorine
Selenium .....	79	80	Bromine
Tellurium .....	125	126.5	Iodine

The student should note that the atomic weight of sulphur is just double the atomic weight of oxygen, and about one-third of the sum of the atomic weights of oxygen and selenium; and the atomic weight of selenium is one-half of the sum of the atomic weights of sulphur and tellurium. Practically analogous conditions obtain among the negative monads.

It should also be observed that the difference between the atomic weight of oxygen and that of sulphur, as well as the difference between the atomic weight of fluorine and that of chlorine, is 16 — the number expressing the atomic weight of oxygen, and the difference between the atomic weights of several other pairs of elements of one family.

Whether these interesting coincidences have any special significance or not they are at least good aids to the memory.

It has already been stated that no compound of oxygen and fluorine with each other is known.

Chlorine, bromine and iodine do not exhibit any energetic affinity for oxygen, but they act with intense energy upon the metals and upon many hydrogen compounds.

Finally, the student should not fail to remember that the dyad salt formers are uniformly dyads only as salt-formers, or, in other words, when they exercise negative polarity; and that the negative monads or halide-formers are uniformly monads only in their rôle of negative radicals.

**572.** After having become acquainted with hydrogen and the salt-formers we may advantageously study nitrogen and phosphorus.

The functions of these elements are altogether different from those of the salt-formers and halide-formers.

The linking functions performed by these non-metallic elements are of great importance, especially those of the nitrogen; and both nitrogen and phosphorus form very strong acids.

Nitrogen forms several highly important compound radicals with hydrogen and oxygen respectively.

Both nitrogen and phosphorus atoms can act as links between atoms of hydrogen and atoms of oxygen, thus possessing both negative and positive bonds, or combining units, at one and the same time.

The range of polarity-values of the nitrogen atom is extraordinary.

**573.** Carbon and silicon will next claim attention.

Carbon, like nitrogen, is chiefly distinguished by its linking functions which are altogether remarkable. Its polyvalence enables carbon atoms tied together in clusters, chains or rings, to serve as skeletons of innumerable compound molecules in organic chemistry, and carbon also forms a large number of important compound radicals with hydrogen and oxygen respectively, or with both.

Carbon may exercise either positive or negative polarity, or both together.

Carbon and silicon are both tetrads and their inorganic compounds therefore present close analogies.

**574.** Boron, being the only remaining non-metallic element, and not to be classed with any other, will be described after carbon and silicon, which it somewhat resembles chemically.

**575.** Next in order we shall consider the elements which seem to occupy a position on the border between the clearly non-metallic elements and the pronouncedly metallic elements.

These elements are the perissads arsenic and antimony. Their

physical properties are metallic, but their chemical properties not so because they combine directly with hydrogen and are incapable of performing basic functions in the formation of salts.

**576.** The parallelisms between elements of the carbon family and those of the nitrogen family are as significant as those shown by the dyad salt formers and the halogens (par. 571):

THE CARBON FAMILY.		THE NITROGEN FAMILY.	
	<i>Atomic weights.</i>		<i>Atomic weights.</i>
Carbon .....	12.	14. ....	Nitrogen
Silicon .....	28.5	31. ....	Phosphorus
Germanium .....	72.5	75. ....	Arsenic
Tin .....	119.	120. ....	Antimony
<hr/>		<hr/>	
Lead .....	206.5	208. ....	Bismuth

**577.** After describing arsenic and antimony, the metallic triads which unite directly with hydrogen and which perform acidic but not basic functions, we shall next consider the metals tin, molybdenum, tungsten and uranium, because they, too, form acids but do not perform basic functions. They differ from arsenic and antimony in that they are incapable of combining directly with hydrogen.

**578.** Then we shall take up the metals that perform basic functions in the formation of salts, beginning with the most feebly basic elements and ending with the alkali metals.

Several of the metals performing basic functions are also capable of performing acidic functions. In such cases it is usually found that the metal exercises a higher polarity-value as an acidic element than it possesses when performing the basic function. Thus acidic chromium is a hexad while basic chromium is either a triad or a dyad, and acidic manganese is either a hexad or a heptad, while basic manganese is a dyad.

After describing the alkali metals and their compounds we will discuss the compounds of ammonium because of the general resemblance between the ammonium salts and the salts of potassium and sodium.

**579.** The **light metals** are those whose specific weights are less than 5 and lower than the specific weights of their own oxides. The most important light metals are lithium, sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium, barium and aluminum.

The **heavy metals** are those whose specific weights are more than 5 and higher than the specific weights of their oxides.

**580.** A comparative exhibit of the univalent and bivalent light metals—the “alkali metals” and the “alkaline-earth metals”—arranged in the order of their atomic weights, is strikingly interesting and instructive. It is as follows:

MONADS.	ALKALI METALS.		DYADS.	ALKALINE-EARTH METALS.	
	<i>Specific weights.</i>	<i>Atomic weights.</i>		<i>Specific weights.</i>	
Cæsium .....	1.5	133	137.5	4	..... Barium
Rubidium .....	1.5	85.5	87.5	2.5	..... Strontium
Potassium .....	0.86	39	40	1.6	..... Calcium
Sodium .....	0.97	23	24.2	1.7	..... Magnesium
Lithium .....	0.6	7	9	2	..... Beryllium

In both groups the intensity of the combining energy of the members is in the order of their atomic weights from highest to lowest. Cæsium is the most pronounced alkali metal, rubidium next, then potassium, sodium, and lithium. The last named alkali metal borders on the alkaline-earth metals, forming a sparingly soluble carbonate.

Of the alkaline-earth metals barium forms the most powerful base and beryllium the weakest, the others standing in just the order of their atomic weights between them.

The atomic weights of the corresponding members of the two respective groups are nearly coincident, and within each group the intervals between the successive atomic weights are either 16 or three times 16.

**581. The alkali metals** are all monads. Their hydroxides are the true alkalies, which are very freely water-soluble.

The sulphides, carbonates and the phosphates of the alkali metals are also readily water-soluble with the exception of those of lithium which are rather sparingly soluble. The alkali carbonates, hydroxides and phosphates are not decomposed by heat.

The salts of the alkali metals with strong acids have a neutral reaction; those with weak acids often have an alkaline reaction.

The alkali metals have such an intense chemical affinity for oxygen that they must be excluded from contact with air; they are, therefore, kept in kerosene or benzin. When brought into contact with water they decompose it, combining with hydroxyl

and liberating one hydrogen atom from each water molecule decomposed. Cæsium decomposes water with the greatest violence; lithium comparatively quietly.

The alkali metals also have an intense affinity for any halogen and for sulphur.

The student should note that while chlorine decomposes water (slowly) by combining with its hydrogen and thus liberating oxygen, the alkali metals unite with hydroxyl and liberate hydrogen from the water.

The oxides of the alkali metals react violently with water, forming hydroxides, or the alkalies.

**582.** The **alkaline-earth metals** are all dyads. Their hydroxides are only sparingly water-soluble. But they have an intense affinity for oxygen and for hydroxyl, and hence decompose water, but not so violently as the alkali metals.

The oxides of the alkaline-earth metals can be preserved for some time in tightly closed bottles.

The normal carbonates and phosphates of the alkaline-earth metals are insoluble in water; but the primary (or acid) phosphates are soluble, and the bicarbonates sparingly soluble. The sulphides are freely soluble.

Their normal salts, when water-soluble, have a neutral reaction. The sulphates and oxalates of barium, strontium and calcium are quite insoluble, but magnesium sulphate is **freely** soluble.

**583.** The alkali metals and the alkaline-earth metals exhibit a greater affinity for oxygen than for sulphur, while the "noble metals" and some other heavy metals show a greater affinity for sulphur than for oxygen.

**584.** After describing briefly the elements and their compounds we shall next briefly describe the family traits, general methods of preparation and modes of identification of the most common and important classes of salts formed by the metals with organic acids.

**585.** For the convenience of the student and to enable him to take up the study of this part of our subject with some definite previous knowledge of what lies before us, the following schedule of the elements and compounds, in the order in which they will be studied, is presented:

- |                                       |                                 |
|---------------------------------------|---------------------------------|
| 1. Hydrogen.                          | 24. Manganese.                  |
| 2. Oxygen.                            | 25. Chromium.                   |
| 3. Fluorine.                          | 26. Iron.                       |
| 4. Chlorine.                          | 27. Aluminum.                   |
| 5. Bromine.                           | 28. Cerium.                     |
| 6. Iodine.                            | 29. Zinc.                       |
| 7. Sulphur.                           | 30. Magnesium.                  |
| 8. Nitrogen.                          | 31. Calcium.                    |
| 9. Phosphorus.                        | 32. Strontium and Barium.       |
| 10. Carbon.                           | 33. Lithium.                    |
| 11. Silicon.                          | 34. Sodium.                     |
| 12. Boron.                            | 35. Potassium.                  |
| 13. Arsenic.                          | 36. Ammonium compounds.         |
| 14. Antimony.                         | 37. Metallic Acetates.          |
| 15. Tin.                              | 38. Metallic Valerates.         |
| 16. Molybdenum, Tungsten and Uranium. | 39. Metallic Oxalates.          |
| 17. Bismuth.                          | 40. Metallic Tartrates.         |
| 18. Platinum and Iridium.             | 41. Metallic Citrates.          |
| 19. Gold.                             | 42. Metallic Lactates.          |
| 20. Silver.                           | 43. Metallic Salicylates.       |
| 21. Mercury.                          | 44. Metallic Phenolsulphonates. |
| 22. Copper.                           | 45. Metallic Benzoates.         |
| 23. Lead.                             | 46. Metallic Oleates.           |

**586.** Full descriptions of the methods of preparation and of the properties of important inorganic substances are given in Vol. II.

## CHAPTER XXIX.

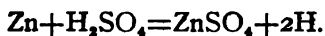
### HYDROGEN.

Symbol, H. At.w., 1. Polarity-value, +1.

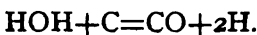
**587. Occurrence in nature.** Hydrogen exists in nature in the free state only in very small quantities; but combined hydrogen constitutes about 1 per cent of the whole mass of the earth. Its most abundant compound is its hydroxide (or oxide), called water, which is composed of one-ninth by weight of hydrogen and eight-ninths of oxygen. Hydrogen is also a constituent of nearly all of the carbon compounds of the animal and vegetable world, and of "coal oil," "natural gas" and bituminous products.

**588. Preparation.** The most convenient and satisfactory method of preparing hydrogen is by the action of zinc upon dilute sulphuric acid. The metal forms zinc sulphate which dissolves in the water contained in the dilute acid, and the hydrogen of the hydroxyl of the acid is displaced by the zinc and passes out of the liquid, being insoluble in it. The gas may be easily collected if the bottle or flask in which it is generated be provided with a perforated stopper into which is fitted a tube through which the hydrogen can be conducted into a jar, bottle, rubber bag or other suitable container, or conveyed wherever it may be required.

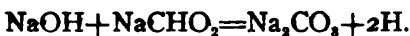
The reaction is:



On a larger scale hydrogen is produced together with carbon monoxide in the manufacture of a "fuel gas" by the decomposition of water, effected by passing steam over coal heated to an intense temperature:



When perfectly pure hydrogen is required it is best to make it by the action of sodium hydroxide upon sodium formiate:



**589. Description.** Hydrogen is a colorless, odorless, tasteless, inflammable gas. It is the lightest of all kinds of matter, occupying nearly  $14\frac{1}{2}$  times as much space as is taken up by an equal weight of air, and about 11,160 times as much as occupied by the same weight of water.

One cubic-decimeter of pure hydrogen at  $0^{\circ}$  C., bar. 760 mm., has been estimated to weigh about 0.09 Gm. The density of hydrogen expressed in units of the density of *dry air* is about 0.0693. The density of *ordinary air*, expressed in hydrogen units, is most commonly stated to be about 14.43. One gram of hydrogen at  $0^{\circ}$  C., bar. 760 mm., occupies about 11.16 cubic-decimeters.

At a temperature estimated to be below  $-200^{\circ}$  and under a pressure of 40 atmospheres hydrogen has been obtained in liquid form.

It is very slightly soluble in water (practically insoluble).

**590. Chemical properties.** The hydrogen molecule is  $H_2$ . At ordinary temperatures hydrogen displays little chemical energy except in its nascent state. Under the influence of strong light, however, it combines slowly, even at ordinary temperatures, with chlorine and bromine. A mixture of hydrogen and chlorine may be exploded by an electric spark; the two elements then unite to form hydrogen chloride. A water-solution of HCl is commonly called hydrochloric acid.

At high temperatures, or by ignition, mixtures of hydrogen and oxygen, or of hydrogen and air, or of hydrogen and chlorine, explode with great violence.

The most intense heat that can be produced by combustion is obtained through the "oxy-hydrogen blow pipe" by means of which a mixture of hydrogen and oxygen in proper proportions is burnt, the product of the combustion being water.

Hydrogen has at high temperatures a sufficiently great affinity for oxygen to act as an effective reducing agent, removing oxygen from oxides, hydroxides, and other oxygen compounds by combining with it to form water.

The tendency of hydrogen to form water is so great that when hydrogen and oxygen are both contained in chemical compounds, particularly in hydroxyl compounds, water is often formed and split off on comparatively slight provocation.

Chlorine (and also oxygen to a great extent) owes its marked

disinfectant power to its affinity for hydrogen whereby unstable and noxious organic substances containing hydrogen are destroyed when brought under its action.

Hydrogen is invariably a monad and of positive chemical polarity in all its compounds. It forms chemical compounds with all the non-metallic elements, but does not unite chemically with any metallic elements except arsenic and antimony. It forms alloys with a few metals, notably palladium.

Hydrogen is contained in all acids, and it may be said that hydrogen performs basic functions in the hydroxyl acids, for the difference between a hydroxyl acid and any one of its metallic salts is that the acid contains hydrogen in the place of the metal. The difference between metallic halides and the hydrogen acids is the same—i. e., a salt or a halide are formed whenever a hydroxyl acid or a hydrogen acid exchanges its basic hydrogen for a metal. The acids are accordingly referred to as the "salts of hydrogen." For these and other reasons hydrogen is sometimes spoken of as "the gaseous metal."

It was once thought that the acid or sour property of acids was due to the oxygen they contained, and that element received its name in consonance with that idea. But as the hydrogen acids which do not contain any oxygen are as decidedly acid as the hydroxyl acids, the notion that oxygen caused the acidity was abandoned and it was instead suggested that hydrogen must be the cause of it. This supposition is as erroneous as the other, for the metallic hydroxides performing basic functions, including the alkalis which possess properties the very opposite of acidic, contain both hydrogen and oxygen. The truth must be that the acid character of all inorganic acids is derived from the acid-forming elements combined with the hydrogen or with the hydrogen and oxygen, and the acidity of the organic acids is derived from the acid-forming compound radicals which, respectively, determine their individuality; while the alkaline character of the hydroxides of the alkali metals and other metals must be in each case determined by the metallic element.

No one atom of any kind can unite directly with more than four hydrogen atoms, and the maximum number of units of negative combining value of any element, under any circumstances, is 4.

**591. Compounds.** The structure of the binary compounds formed by hydrogen is sufficiently illustrated by the following:

HF, Hydrogen fluoride or hydrofluoric acid.

HCl, Hydrogen chloride or hydrochloric acid.

HBr, Hydrogen bromide or hydrobromic acid.

HI, Hydrogen iodide or hydriodic acid.

HOH, or  $H_2O$ , Hydrogen hydroxide, or hydrogen oxide, or water.

HS $H$ , or  $H_2S$ , Hydrogen hydrosulphide, or hydrogen sulphide.

HSe $H$ , or  $H_2Se$ , Hydrogen hydroselenide, or hydrogen selenide.

HTe $H$ , or  $H_2Te$ , Hydrogen hydrotelluride, or hydrogen telluride.

$H_3N$ , Hydrogen nitride, or ammonia.

$H_3P$ , Hydrogen phosphide, or phosphine.

$H_3As$ , Hydrogen arsenide, or arsine.

$H_3Sb$ , Hydrogen antimonide, or stibine.

$H_3B$ , Hydrogen boride.

$H_4C$ , Hydrogen carbide, methane, or marsh gas.

$H_4Si$ , Hydrogen silicide.

The compounds of hydrogen with the halogens are the *hydrogen acids*.

Hydrogen dioxide,  $H_2O_2$ , [or HO.OH, or  $(HO)_2$ ] is an unstable compound, readily giving up one-half of its oxygen and thereby reduced to water. It is, therefore, a powerful *oxidizing agent*. A water solution of it is commonly called "peroxide of hydrogen."

Hydrogen disulphide,  $H_2S_2$ , is also known.

With carbon hydrogen forms a large number of compounds called hydrocarbons, in which the carbon atoms are united to each other in chains or rings.

Hydrogen is contained in all acids, acid salts, hydroxides, hydrocarbons, carbohydrates, alcohols, ethers, esthers, aldehydes, ketones, volatile oils, camphors, alkaloids, and many other important classes of substances.

The most important compound radical formed by hydrogen is hydroxyl, HO. The compound radicals formed by carbon and hydrogen are many; they are briefly referred to under carbon. The radicals  $H_4N$ ,  $H_2N$ , HN and HS are also of common occurrence.

592. As hydrogen of all elements has the lowest atomic

weight, and of all substances the lowest specific weight, and as it has a uniform valence as low as that of any other element, it has been adopted as the standard of comparison and unit of expression of all such values. Thus the atomic weight of hydrogen is 1, its specific weight is 1, and its valence is 1. The atomic weight of any element having gaseous diatomic molecules is coincident with its vapor density expressed in units of the density of hydrogen.

593. While it is correct to say that the combining value of the hydrogen atom is numerically 1, and that all monad atoms have in a sense the same combining value, while dyads have twice that value, triads three times that value, etc., the student must not lose sight of the fact that the *quality* of the combining power of hydrogen, and the functions it performs in the formation of compounds, invest it with a character so unique that altogether erroneous notions might easily arise from the thoughtless employment of such expressions as the not uncommon one that monad atoms are those capable of "taking the place of hydrogen," atom for atom, that a dyad atom can "take the place of two hydrogen atoms," etc., whereas the fact is that not one of the non-metallic elements can ever *take the place of hydrogen* in any compound without a most radical alteration of its general character.

## CHAPTER XXX.

### OXYGEN.

Symbol, O. At.w., 16. Polarity-value, —2.

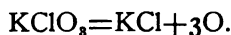
**594. Occurrence.** Oxygen constitutes about one-half of the whole mass of the globe. In its uncombined state it exists in the atmosphere which is a mixture of one-fifth by weight of oxygen and four-fifths of nitrogen, together with very small amounts of moisture and carbon dioxide. Water is composed of eight-ninths of its weight of oxygen and one-ninth of hydrogen. Nearly one-half of the weight of the rocks is oxygen. Oxygen also enters to a large extent into the composition of the substances of which the soils, plants and animal bodies consist.

**595. Preparation.** Certain oxygen compounds are easily decomposed, by heat or otherwise, giving up the whole or a part of their oxygen. Mercuric oxide,  $\text{HgO}$ , and potassium chlorate,  $\text{KClO}_3$ , surrender all of their oxygen under the influence of heat; manganese dioxide,  $\text{MnO}_2$ , one-third of its oxygen:



barium dioxide,  $\text{BaO}_2$ , and lead dioxide,  $\text{PbO}_2$ , give up one-half of their oxygen.

The most common and satisfactory method is to heat a mixture of potassium chlorate with one-fourth of its weight of manganese dioxide, when the chlorate alone decomposes:



The manganese dioxide greatly facilitates the quiet and yet rapid dissociation of the chlorate, but does not seem to take part in the reaction as it remains intact after all of the potassium chlorate has been converted into chloride. But the manganese dioxide employed for this purpose must be pure. Manganese dioxide in powder is said to be sometimes adulterated with charcoal and this when mixed with the potassium chlorate makes an explosive mixture.

**596. Description.** Oxygen is a colorless, odorless, tasteless, non-inflammable gas. At a temperature of about  $120^{\circ}$  and under a pressure of 50 atmospheres it becomes liquid. It is very slightly soluble in water.

One cubic-decimeter of pure oxygen at  $0^{\circ}$  C., bar. 760 mm., has been estimated to weigh about 1.43 Gm. One Gm of oxygen under the conditions stated occupies a volume of about 699 cubic-centimeters.

The density of oxygen expressed in units of the density of dry air is about 1.105.

One cubic-decimeter of *dry air*, free from carbon dioxide,  $\text{CO}_2$ , at  $0^{\circ}$  C., under 760 mm. pressure, weighs 1.29303 Gm. *Ordinary air* weighs less. At  $0^{\circ}$  C. ordinary air weighs 0.00075 less than dry air; but the difference increases with the temperature, and at  $62^{\circ}$  F., bar. at 30 inches, ordinary air has been estimated to weigh about 0.005 less than dry air, so that in order to reduce the weight of dry air to the corresponding weight of the same volume of air in its ordinary condition of humidity it must be multiplied by 0.995.

The weight of one cubic-decimeter of ordinary air at  $0^{\circ}$  C. is 1.29303 Gm  $\times$  0.99925.

The co-efficient of expansion of any gas or of any mixture of gases is 0.003665 of its volume for each degree C.

At  $16^{\circ}.67$  C. ( $62^{\circ}$  F.) one cubic-decimeter of *dry air* weighs 1.21858 Gm, and one cubic-decimeter of *ordinary air* weighs 1.21858 Gm  $\times$  0.995.

The vapor density of oxygen at  $0^{\circ}$  C., bar. 760 mm., is 15.88; that of nitrogen is 14.01; that of carbon dioxide is 26.945; and the vapor density of water vapor is 8.98.

**597. Chemical properties.** Oxygen is invariably of negative polarity in all its compounds and always a dyad.

Every element except fluorine is capable of uniting directly with oxygen.

The binary compounds formed by other elements with oxygen are called oxides.

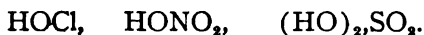
No one atom of another element can combine directly with more than 4 oxygen atoms. A higher valence than 6 is never exhibited by any element except in combination with oxygen.

Ordinary oxygen is  $\text{O}_2$ ; ozone is  $\text{O}_3$ .

At ordinary temperatures oxygen exhibits no great chemical

energy, as we know from the fact that the air constantly contains over twenty per cent of uncombined oxygen. But many elements are oxidized or "attacked by oxygen" at higher temperatures. At still higher temperatures, however, many oxides decompose.

The extent to which oxygen performs the function of linking other atoms together is remarkable. This linking function is strikingly manifest in all true acids, bases and salts. In the hydroxyl acids the hydrogen of the hydroxyl is not directly united to the acidic element, but oxygen occupies a position between the hydrogen and the acid-forming element as the link by which they are held together. In bases oxygen is the link between the metal and the hydrogen. In salts oxygen links the element performing the basic function to the acidic element. These several conditions are illustrated by the following formulas:



Oxygen also enters into the composition of the alcohols, aldehydes, ketones, ethers, acids and salts of organic chemistry.

Whenever two oxygen atoms are directly united to each other in any compound it follows that the polarity-value of one of them must be 0.

**598. Oxidation** in a restricted sense means combination with oxygen. Whenever any element takes up oxygen by chemically combining with it, that element is said to be oxidized or to undergo oxidation. An increase of the proportion of oxygen held in combination by any atom or group of atoms is also called oxidation, as the change of a lower oxide to a higher oxide.

The opposite of oxidation is *reduction*.

In a wider sense the term oxidation means an increase of polarity-value, or an increase of positive bonds, or a decrease of negative bonds.

The variations in the polarity-value of elements, commonly called "variable valence," occur principally in the compounds they form with oxygen.

The oxygen of the air, being uncombined, has a polarity-value of 0. Therefore, whenever it combines with any other element and thus assumes a polarity-value of  $-2$  every oxygen atom transfers two units of polarity-value to the element with which it combines; and when two or more oxygen atoms enter into direct combination with one or more atoms of any other element the latter may attain a higher polarity-value than it can acquire in any other way. All of our most powerful oxidizing agents such as the nitrates, chlorates, chromates and permanganates, are either acids or salts in which the acidic element exercises a high polarity-value imparted to it primarily by the oxygen of the air.

*Combustion* in oxygen, or in air, is generally understood to mean rapid oxidation accompanied by great heat.

Gaseous elements which, like oxygen, support combustion, or chemical combination accompanied by heat and light, are called combustors. Chlorine is one of the active combustors.

Fire is combustion. But "slow combustion" is also a common expression and applies to slow oxidation which does not produce a high temperature and is unattended by the evolution of light.

The following examples of combustion in air are sufficient:

When hydrogen is ignited the product of its fierce combustion is water:  $2\text{H} + \text{O} = \text{H}_2\text{O}$ .

When sulphur burns the product is the very irritating gas called sulphur dioxide:  $\text{S} + 2\text{O} = \text{SO}_2$ .

When phosphorus is ignited it oxidizes at the expense of the oxygen of the air to phosphorus pentoxide, a white solid which forms phosphoric acid with water:  $2\text{P} + 5\text{O} = \text{P}_2\text{O}_5$ .

When carbon undergoes combustion it forms  $\text{CO}_2$  if the supply of air or oxygen is plentiful, but  $\text{CO}$  if the supply of oxygen is limited.

**599.** Ozone is  $\text{O}_3$ , or



consisting of triatomic molecules of oxygen, produced by the action of electricity upon the ordinary or diatomic molecules of that element. Small amounts of ozone always exist in the air, but especially immediately after thunderstorms.

It is a colorless gas having a density one-half greater than that of ordinary oxygen. Its odor is peculiar.

The molecules of ozone are easily split up into normal or diatomic molecules of oxygen and free oxygen atoms, which, in their nascent state, have great chemical energy, vigorously oxidizing a number of metals and attacking various other substances. Ozone thus decomposes potassium iodide, liberating the iodine from it.

**600. Compounds.** The most important compounds of oxygen are the oxides, the bases, hydroxyl acids and other hydroxides; the oxygen salts; and, in organic chemistry, the alcohols, ethers, esthers, aldehydes, ketones, organic acids, most of the alkaloids, etc.

All the metallic oxides are solids, and solid non-metallic oxides also exist, as, for instance,  $\text{SO}_3$ ,  $\text{SiO}_2$ ,  $\text{N}_2\text{O}_5$  and  $\text{P}_2\text{O}_5$ .

Among the liquid oxides are water, hydrogen dioxide, and phosphorous anhydride.

Examples of gaseous oxides are  $\text{Cl}_2\text{O}$ ,  $\text{Cl}_2\text{O}_4$ ,  $\text{SO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{NO}_2$  (or  $\text{N}_2\text{O}_4$ ),  $\text{CO}$ , and  $\text{CO}_2$ .

The structure of oxides is shown in Chapter XI, par. 251 to 255, and their classification into acidic oxides, basic oxides and indifferent oxides there discussed.

**601.** The **official metallic oxides** are the following:

$\text{Ag}_2\text{O}$ , Silver oxide; *argenti oxidum*. Dark brown powder. Insoluble.

$\text{Hg}_2\text{O}$ , Mercurous oxide; *hydrargyri oxidum nigrum*. Black powder. Insoluble.

$\text{CaO}$ , Calcium oxide; *calcii oxidum*. Commonly called lime. White.

$\text{BaO}$ , Barium oxide; *barii oxidum*. Commonly called "baryta." White.

$\text{MgO}$ , Magnesium oxide; *magnesii oxidum*. Called "Magnesia" in the *Pharmacopœia*. White powder. Insoluble.

$\text{ZnO}$ , Zinc oxide; *zinci oxidum*. White powder. Insoluble.

$\text{PbO}$ , Lead oxide; *plumbi oxidum*. "Litharge" and "Massicot" are both  $\text{PbO}$ . Red or yellow powder. Insoluble.

$\text{CuO}$ , Copper oxide; *cupri oxidum*. Black powder. Insoluble.

$\text{HgO}$ , Mercuric oxide; *hydrargyri oxidum rubrum*, and *hydrargyri oxidum flavum*. The red oxide of mer-

cury is still frequently called "red precipitate," and the precipitated oxide is the one called yellow oxide of mercury.

$\text{BaO}_2$ , Barium dioxide; *barii dioxidum*. Grayish-white.

$\text{Fe}_2\text{O}_3$ , Ferric oxide; *ferri oxidum*. Red-brown powder. Insoluble.

$\text{Bi}_2\text{O}_3$ , Bismuth trioxide; *bismuthi oxidum*. White powder. Insoluble.

$\text{As}_2\text{O}_3$  (or  $\text{As}_4\text{O}_6$ ), Arsenous oxide; *arseni oxidum*. Called "arsenous acid," *acidum arsenosum*, in the *Pharmacopœia*. White or colorless. Sparingly water-soluble, forming acid.

$\text{Sb}_2\text{O}_3$ , Antimonous oxide; *antimoni oxidum*. White or colorless. Insoluble.

$\text{MnO}_2$ , Manganese dioxide; *mangani dioxidum*; black oxide of manganese. Insoluble.

$\text{PbO}_2$ , Lead dioxide; *plumbi dioxidum*. Red powder. Insoluble.

$\text{CrO}_3$ , Chromic anhydride; *chromicum anhydridum*. Called chromic acid, *acidum chromicum*, in the *Pharmacopœia*. Dark red crystals. Readily water-soluble, forming acid.

All of the metallic oxides may be said to be insoluble in water, because the only metallic oxides which form solutions with water react with it to form either acids or bases.

Because of their insolubility several of the metallic oxides can be made by precipitation; others are made by the dissociation of carbonates by strong heat, this method being called calcination; other metallic oxides are made by the combustion or oxidation of the metals in air or in oxygen.

Chromic anhydride is prepared by the decomposition of potassium dichromate with sulphuric acid.

The trioxides of arsenic and antimony can be produced by roasting the sulphides. The arsenous oxide, being volatile, is condensed in chambers; the antimonous oxide is obtained as a fixed residue when the antimonous sulphide is roasted.

**602. Official Metallic Hydroxides.** The only *freely water-soluble* metallic hydroxides are those of potassium and sodium.

The hydroxides of barium, strontium and calcium are *sparingly soluble*.

All the water-soluble hydroxides exhibit a strongly alkaline reaction on litmus paper.

The hydroxides of all the metals except those of the alkalis and alkaline earths are *insoluble* in water.

The following metallic hydroxides are official:

KOH, Potassium hydroxide; potassii hydroxidum. Called "potassa" in the Pharmacopœia, and commonly spoken of as "caustic potash." Also called "potassium hydrate." White solid. Extremely freely soluble; deliquescent.

NaOH, Sodium hydroxide; sodii hydroxidum. Called "Soda" in the Pharmacopœia, and also commonly called "caustic soda." Also called "sodium hydrate." White solid. Extremely freely soluble.

Ba(OH)<sub>2</sub>, Barium hydroxide; barii hydroxidum. White. Not freely soluble.

Ca(OH)<sub>2</sub>, Calcium hydroxide; calcii hydroxidum. White. Very sparingly soluble.

Al(OH)<sub>3</sub>, Aluminum hydroxide; alumini hydroxidum. Called "aluminum hydrate," alumini hydras, in the Pharmacopœia. Insoluble white powder.

Fe(OH)<sub>3</sub>, Ferric hydroxide; ferricum hydroxidum. Called "hydrated sesquioxide or oxide of iron" and "ferric hydrate." Red-brown, insoluble powder.

The hydroxides of potassium and sodium are produced by metathesis, the alkali carbonates being treated, in solution, with calcium hydroxide, the bye-product being calcium carbonate.

The hydroxides of barium, strontium, calcium and magnesium can be made by adding water to their oxides.

All insoluble metallic hydroxides, like those of magnesium, zinc, aluminum, iron, lead, and copper, can be made by precipitation from water-soluble salts of the respective metals.

## CHAPTER XXXI.

### FLUORINE.

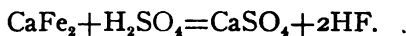
Symbol, F. At. w., 19. Polarity-value, —1.

**603.** Fluorine occurs in the form of calcium fluoride or *fluor-spar*,  $\text{CaF}_2$ , and as *cryolite*,  $\text{AlF}_3 \cdot 3\text{NaF}$ , which is a double fluoride of aluminum and sodium.

In the free state this element is a greenish-yellow gas; but very little is known concerning the properties of free fluorine because the intensity of its chemical energy is so great that it can not be retained in an uncombined state long enough to study it.

No compound of fluorine is known in which that element exercises positive polarity. It is the only element which does not combine with oxygen.

Its most important and interesting compound is hydrofluoric acid, HF, which is obtained by decomposing calcium fluoride with strong sulphuric acid:



*Hydrofluoric acid* is a colorless, fuming, highly corrosive liquid, very poisonous because of its destructive chemical action. It forms silicon fluoride when it comes in contact with silica and silicates and is, therefore, employed to produce etchings on glass. Owing to its action on glass it must be kept in caoutchouc bottles.

For further information regarding fluorine and the fluorides, see Chapter XI, par. 245 and 246.

## CHAPTER XXXII.

### CHLORINE.

Symbol, Cl. At. w., 35.4.

**604. Occurrence.** Chlorine does not occur in the free state, but abundantly in combination with sodium as common salt (sodium chloride) in sea-water and salt-springs, and in salt beds or mines as rock salt. It also occurs as *carnallite*, a "double chloride of potassium and magnesium,"  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , in the salt-beds at Stassfurth, Germany.

**605. Preparation.** Chlorine is most commonly prepared by heating manganese dioxide with hydrochloric acid:

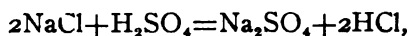


But it will be seen from this equation that only one-half of the chlorine of the hydrochloric acid is liberated, the remainder forming manganese chloride.

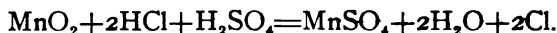
Another method consists in heating a mixture of manganese dioxide, sodium chloride and sulphuric acid. These materials are cheaper and all the chlorine is liberated.



This equation may be separated into two parts, representing two successive reactions, namely:



and then



Chlorine may be obtained in water-solution, with potassium chloride, for medicinal uses and for certain other purposes where the presence of the chloride of potassium is unobjectionable, by adding potassium chlorate to hydrochloric acid:



But the liberation of the chlorine by this reaction is very slow unless the hydrochloric acid be concentrated and the mixture heated.

When chlorine is required for disinfecting sick-rooms, etc., it may be expeditiously generated from chlorinated lime by adding diluted sulphuric or hydrochloric acid, or vinegar.

**606. Description.** Chlorine is a yellowish-green gas of suffocating characteristic odor, poisonous when inhaled in considerable quantities.

At 15° C. it can be compressed into a liquid under the pressure of four atmospheres.

One volume of water at 15° C. dissolves about 2½ volumes of chlorine. A water-solution saturated at 10° C. contains about 0.6 per cent of chlorine. Chlorine water will be fully treated of in Vol. II.

One cubic-decimeter of chlorine at 0° C., under the pressure of one atmosphere, weighs about 3.17 Gm.

**607. Chemical properties.** The polarity-value of chlorine is -1 in all chlorides; but when chlorine exercises positive polarity its polarity-value may be +1, as in the hypochlorites; or +3, as in the chlorites; or +5, as in the chlorates; or +7, as in the perchlorates.

No one atom of any other element can unite with more than 6 atoms of chlorine.

The molecule of chlorine is diatomic at lower temperatures; but monatomic at higher temperatures.

Chlorine displays great intensity of chemical energy and forms very stable halides with strongly positive elements. But the compounds in which chlorine exercises positive polarity (being directly united to oxygen) are comparatively unstable. Some of the non-metallic chlorides are liable to decompose with explosive violence.

Chlorine unites with all other elements. It displaces bromine and iodine from their compounds.

The affinity of chlorine for hydrogen is so great that it removes that element from many of its compounds; the reaction by which this is accomplished is one of substitution, one chlorine atom uniting with the hydrogen atom while another chlorine atom is inserted into the molecule from which the hydrogen was re-

moved, thus, in most cases, completely changing the general character and properties of the molecule.

Chlorine has the power also to decompose water uniting with its hydrogen and thus liberating the oxygen, which, in its nascent state, vigorously attacks and decomposes or oxidizes other substances. Noxious effluvia and other poisonous organic substances are frequently unstable hydrogen compounds which may be destroyed or rendered innocuous by decomposition or oxidation, and the great disinfectant power of chlorine is thus accounted for.

Unstable chlorine compounds, such as readily give up their chlorine (or their oxygen if they contain both chlorine and oxygen) are, therefore, also employed as disinfectants and as oxidizing agents.

Potassium chlorate is one of the most powerful oxidizing agents on account of the high polarity-value of its chlorine atom.

The *nitrohydrochloric acid* of the pharmacopœias, and the *aqua regia* of the chemists, depend for their uses upon the free chlorine which they contain. This chlorine is formed according to the following reactions:



and



Aqua regia is usually a mixture made of one part of strong nitric acid and from three to five parts of strong hydrochloric acid. It dissolves gold and platinum, forming chlorides. These metals are insoluble in all acids.

**608. Compounds.** Hydrogen and chlorine form together but one compound, HCl, hydrogen chloride or *hydrochloric acid*. It is one of the most powerful and useful of the acids.

The *oxides of chlorine* are chlorine monoxide, Cl<sub>2</sub>O, which forms hypochlorous acid when dissolved in water; and chlorine dioxide, ClO<sub>2</sub>. They are extremely unstable.

The acids formed by chlorine are:

HClO, or HOCl, Hypochlorous acid.

HClO<sub>2</sub>, or HOClO, Chlorous acid.

HClO<sub>3</sub>, or HOClO<sub>2</sub>, Chloric acid.

HClO<sub>4</sub>, or HOClO<sub>3</sub>, Perchloric acid.

Chlorous acid is known only through a few of its salts.

**609. Chlorides.** Chlorine and the chlorides have been referred to and the structure of the chlorides illustrated in Chapter XI, par. 245 and 247.

The officinal chlorides are:

HCl, Hydrogen chloride, or hydrochloric acid; acidum hydrochloricum. In water-solution, colorless.

KCl, Potassium chloride; potassii chloridum. Colorless or white crystals. Soluble.

NaCl, Sodium chloride; sodii chloridum. "Salt." Colorless or white, crystalline, soluble.

LiCl, Lithium chloride; lithii chloridum. White; soluble.

H<sub>4</sub>NCl, Ammonium chloride; ammonii chloridum. Sal ammoniac. White, crystalline, soluble.

HgH<sub>2</sub>NCl, Mercurammonium chloride, or "ammoniated mercury;" hydrargyrum ammoniatum. Called also "white precipitate." Probably HgClNH<sub>2</sub>, mercuric chloramide. White, insoluble powder.

BaCl<sub>2</sub>, Barium chloride; barii chloridum. White, crystalline; soluble.

SrCl<sub>2</sub>, Strontium chloride; strontii chloridum. White, crystalline; soluble.

CaCl<sub>2</sub>, Calcium chloride; calcii chloridum. White amorphous when fused and anhydrous; extremely freely soluble, deliquescent.

MgCl<sub>2</sub>, Magnesium chloride; magnesii chloridum. White, crystalline; readily soluble.

ZnCl<sub>2</sub>, Zinc chloride; zinci chloridum. White crystalline or granular. Extremely readily soluble; deliquescent.

AlCl<sub>3</sub>, Aluminum chloride; alumini chloridum. White, crystalline. Very easily soluble.

FeCl<sub>3</sub>, Ferric chloride; ferricum chloridum, or ferri chloridum, frequently called "sesquichloride of iron," "perchloride of iron" and even "muriate of iron." Orange-yellow or red, crystalline. Extremely readily soluble in either water or alcohol. Very hygroscopic.

HgCl, Mercurous chloride; hydrargyri chloridum mite; calomel. White, insoluble powder.

- $\text{HgCl}_2$ , Mercuric chloride; hydrargyri chloridum corrosivum, "corrosive sublimate." White or colorless, crystalline. Soluble.
- $\text{AuCl}_3$ , Gold trichloride; auri chloridum. The officinal preparation is mixed with sodium chloride. Golden yellow, crystalline. Readily soluble.
- $\text{OBiCl}_2$ , Bismuthyl chloride, or "oxychloride of bismuth; bismuthi oxychloridum. White, insoluble powder.
- $\text{O}_3\text{Sb}_2\text{Cl}_7$ , Antimony oxychloride; antimoni oxychloridum. Algaroth's powder. White. Insoluble.
- $\text{SbCl}_3$ , Antimony trichloride; antimoni trichloridum. Butter-like solid. Decomposed by water.
- $\text{PtCl}_4$ , Platinic chloride; platini chloridum. Red-brown, crystalline, deliquescent. Readily soluble, forming a yellowish-red solution.

Solutions of zinc chloride and ferric chloride are also officinal; and a solution of chloride of antimony in England.

*Solubility.* All the chlorides enumerated in the foregoing table are water-soluble except ammoniated mercury, calomel, oxychloride of bismuth and oxychloride of antimony, which are quite insoluble. Antimony trichloride is decomposed by water but is soluble in hydrochloric acid.

*Preparation.* Water-soluble chlorides are generally prepared by saturating hydrochloric acid with the metals or their oxides, hydroxides or carbonates.

Calomel and mercuric chloride, being volatile, are made by sublimation from the sulphates of mercury with sodium chloride.

All insoluble metallic chlorides, such as silver chloride, mercurous chloride, etc., can be made by precipitation from soluble mercury salts with sodium chloride.

**610. Reactions of chlorides.** Solutions of hydrochloric acid and other water-soluble chlorides produce with solution of silver nitrate a white curdy precipitate of silver chloride, soluble in ammonia water. Silver chloride is insoluble in acids as well as in water, and hence the curdy precipitate is obtained even when the solution is strongly acidulated with nitric acid before the silver nitrate is added.

The insoluble chlorides yield sodium chloride when heated to redness with sodium carbonate.

When chlorides are heated with dilute sulphuric acid, hydrochloric acid is formed. If manganese dioxide is added at the same time, free chlorine is given off.

**611. Hypochlorites** are the salts of  $\text{HOCl}$ , which is a normal acid. They are produced by the action of chlorine upon the alkalis.

$\text{KClO}$ , Potassium hypochlorite, is the chief constituent of "Javelle Water." White, hygroscopic, readily soluble.

$\text{NaClO}$ , Sodium hypochlorite, is the effective constituent of the official solutions of "chlorinated soda," or "Labarraque's solution." White; readily soluble.

$\text{Ca}(\text{ClO})_2$ , Calcium hypochlorite, is the important constituent of "chlorinated lime," which is popularly called "chloride of lime," or "bleaching powder." White powder. Hygroscopic; soluble.

These hypochlorites are water-soluble. They are unstable, giving off chlorine as they decompose, and their uses as disinfectants depend upon the quantity of "available chlorine" they liberate upon the addition of an acid.

**612. Chlorates.** Chloric acid is a di-meta-acid. The only official chlorates are those of potassium and sodium:

$\text{KClO}_3$ , Potassium chlorate; potassii chloras. White or colorless crystalline. Water-soluble.

$\text{NaClO}_3$ , Sodium chlorate; sodii chloras. White or colorless, crystalline. Soluble.

Both are official as well as officinal. They are produced by passing chlorine into a liquid containing the chloride of the alkali metal together with calcium hydroxide.

Potassium chlorate is soluble in about 16 parts of water and sodium chlorate in about 1.1 parts.

Chlorates are very unstable, exploding violently by percussion, or when triturated with reducing agents, or when heated rapidly and strongly or ignited. Sufficient heat reduces them to chlorides, all the oxygen being expelled.

Chlorates are changed to chlorides also by the action of hydrochloric acid, chlorine being then liberated and water formed.

## CHAPTER XXXIII.

### BROMINE.

Symbol, Br. At. w., 80.

**613. Occurrence.** Bromine occurs in sea-water and in salt-springs in the form of magnesium bromide,  $\text{MgBr}_2$ , and bromides also occur in the salt beds at Kreuznach and Stassfurth, Germany.

**614. Preparation.** Bromine is liberated from the bromides by chlorine, which, being a more powerful negative element, displaces the bromine. On a smaller scale bromine may also be obtained from bromides, in the same manner as chlorine from chlorides, by the aid of manganese dioxide and sulphuric acid:



**615. Description.** Bromine is a dark brownish-red, mobile liquid which gives off suffocating yellowish-red vapors, intensely irritating to the eyes and the respiratory organs and poisonous when inhaled. The odor of bromine is much like that of chlorine but more intense. The sp. w. of bromine is about 3 (Water=1). It is soluble in from 30 to 35 parts of water, forming an orange-red solution called "bromine water."

Bromine is readily soluble in alcohol and in ether, but attacks these liquids chemically and sometimes so vigorously as to cause effervescence from the vapors of bromine, ethyl bromide and alcohol or ether, the heat generated by the reaction being sufficient to vaporize them. Carbon disulphide and chloroform also dissolve bromine.

Strong solutions of bromine may be prepared for surgical uses by dissolving the bromine in strong solutions of potassium bromide.

Bromine will be referred to again in Vol. II.

**616. Chemical properties.** Bromine exhibits intense chemical energy, next to chlorine among the halogens. It decomposes water, taking the hydrogen from it, and is a powerful disinfect-

ant. Its compounds are analogous to those formed by chlorine, and the chlorides and bromides of any one metal are isomorphous. Bromides are generally less stable compounds than the chlorides, but more stable than the iodides. Bromine is displaced by chlorine, but displaces iodine.

Bromine forms monatomic molecules at very high temperatures but diatomic molecules at lower temperatures. In this it resembles chlorine and iodine.

The polarity-value of bromine in bromides is  $-1$ ; in hypobromites it has a polarity-value of  $+1$ , and in bromates of  $+5$ . The hydroxyl acids and their salts are less stable than the halides.

**617. Compounds.** Hydrogen bromide is a powerful acid.

No oxide of bromine is known.

Bromine monochloride,  $\text{BrCl}$ , is an unstable yellowish-red liquid.

The structure of the bromides is referred to and illustrated in Chapter XI, par. 245 and 249.

**618. The Official Bromides are:**

$\text{HBr}$ , Hydrogen bromide, or hydrobromic acid; acidum hydrobromicum. Colorless liquid.

$\text{KBr}$ , Potassium bromide; potassii bromidum. White, crystalline. Soluble.

$\text{NaBr}$ , Sodium bromide; sodii bromidum. White, crystalline. Soluble.

$\text{LiBr}$ , Lithium bromide; lithii bromidum. White, crystalline. Soluble.

$\text{H}_4\text{NBr}$ , Ammonium bromide; ammonii bromidum. White, crystalline. Soluble.

$\text{SrBr}_2$ , Strontium bromide; strontii bromidum. White, crystalline. Soluble.

$\text{CaBr}_2$ , Calcium bromide; calcii bromidum. White, crystalline. Freely soluble.

$\text{ZnBr}_2$ , Zinc bromide; zinci bromidum. White, crystalline. Soluble.

$\text{HgBr}_2$ , Mercuric bromide; hydrargyri dibromidum. White, crystalline. Soluble.

$\text{FeBr}_2$ , Ferrous bromide; ferri dibromidum. Pale green, crystalline. Soluble.

Hydrobromic acid is a water-solution containing 10 per cent

of absolute  $\text{HBr}$ . All the others enumerated are solids, and all are water-soluble.

The common insoluble bromides are those of silver and lead, and mercurous bromide.

**619. Methods of preparation.** The *materials* out of which the officinal bromides are made are bromine, hydrobromic acid, bromide of iron, and potassium bromide.

Water-soluble metallic bromides are made from bromine, hydrobromic acid, or iron bromide.

Insoluble metallic bromides are prepared from potassium bromide by precipitation.

Bromides of iron, zinc, and mercury are readily made by synthesis of the metal with bromine under water.

**620. Reactions of bromides.** Water-soluble bromides give a curdy yellowish-white precipitate with silver nitrate solution; this precipitate of silver bromide is difficultly soluble in ammonia water. Chlorine displaces the bromine from the bromides; hence yellowish-red bromine is liberated when a current of chlorine is conducted into a solution of a bromide or when chlorine water is added to such a solution.

When insoluble bromides are heated to redness with sodium carbonate, sodium bromide is formed.

## CHAPTER XXXIV.

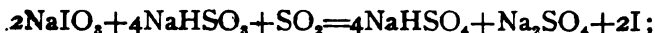
### IODINE.

Symbol, I. At.w., 126.5.

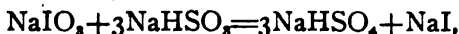
**621. Occurrence and preparation.** Iodine accompanies chlorine and bromine, the halides of these three elements being generally found together in sea-salts and in salt-springs and salt deposits. The ashes of sea-plants contain iodides, and for a long time the only source of iodine consisted of the sea weeds washed up by the storms on the coasts of Scotland, Ireland, Normandy, and elsewhere. The fused ash formed by the burning of these weeds is called "kelp" in Scotland, "varec" in Normandy, and "barilla" in Spain. From the crude iodides separated out of the sea plant ash the iodine is obtained in the same manner as chlorine and bromine are liberated from chlorides and bromides:



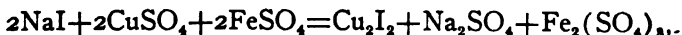
Large quantities of iodine are now obtained from the residues of the mother liquors collected in the process of separating sodium nitrate from the saltpeter deposits of Chili. These residues contain sodium iodate from which the iodine is separated by precipitation:



or by several successive reactions, the first of which results in converting the sodium iodate into sodium iodide:



after which the sodium iodide is converted into cuprous iodide:



and, finally, the cuprous iodide is decomposed and the liberated iodine recovered by sublimation:

- $\text{HgI}_2$ , Mercuric iodide; *hydrargyri iodidum rubrum*. Vermilion colored. Amorphous or crystalline. Nearly insoluble.
- $\text{AsI}_3$ , Arsenous iodide; *arseni iodidum*. Orange-red, crystalline. Readily soluble.
- $\text{OBI}$ , Bismuthyl iodide; *bismuthi oxyiodidum*. White powder. Insoluble.
- $\text{S}_2\text{I}_2$ , Sulphur iodide; *sulphuris iodidum*. Grayish-black, crystalline. Nearly insoluble.

All the beforementioned iodides are solids except hydriodic acid, and all are water-soluble except the iodides of silver, lead, mercury and bismuthyl.

**626. Methods of preparation.** The usual *materials* are iodine, potassium iodide and iron iodide.

The iodides of iron and zinc are made from the respective metals with iodine and water, by synthesis.

The iodides of potassium, sodium, ammonium, calcium and strontium may all be made from iron iodide by metathesis.

Potassium iodide and sodium iodide may also be made from the alkali hydroxides and iodine.

The iodides of sulphur and arsenic are prepared by direct synthesis, the elements being fused together.

Insoluble metallic iodides are made from potassium iodide by precipitation.

The iodides of mercury can also be made by direct synthesis the mercury and iodine being triturated together.

Hydriodic acid is produced by bringing hydrogen sulphide in contact with iodine in water, when the sulphur is precipitated, being displaced by the iodine. It is also made by decomposing potassium iodide with tartaric acid.

**627. Reactions of iodides.** Water-soluble iodides give a light yellow precipitate with silver nitrate solution; this precipitate is silver iodide which is insoluble in ammonia water. If fuming nitric acid or chlorine water be added carefully, drop by drop, to a solution of an iodide, iodine is liberated and may be detected by its odor, or by means of starch mucilage which is colored blue by the iodine; and if the amount of iodine is considerable it is precipitated as a blackish powder or may separate in small crystals on standing.

When heated with sulphuric acid, and more readily in the presence of manganese dioxide, the iodides give off violet vapors of iodine.

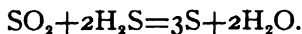
Solutions of the iodides give the odor of iodine and a blue color with starch mucilage on addition of a solution of ferric chloride. They give a yellow precipitate of lead iodide with solutions of lead salts, and scarlet red precipitates of mercuric iodide with mercuric chloride or nitrate.

## CHAPTER XXXV.

### SULPHUR.

Symbol, S. At.w., 32.

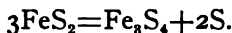
**628. Occurrence.** Native free sulphur occurs in immense quantities in Italy, South America, California, Louisiana, and other places. The sulphur deposits near volcanoes are supposed to have been formed by the interaction upon each other of the sulphur dioxide and the hydrogen sulphide which issue from them:



Sulphur in combination with metals, as sulphides of iron, copper, lead, zinc, occurs in abundance; also sulphates of calcium and barium.

Crude native sulphur is purified by fusion, and more effectively by sublimation.

Sulphur is separated from iron pyrites,  $\text{FeS}_2$ , by heating the broken mineral:



**629. Description.** Sulphur is at ordinary temperatures a light yellow hard solid, odorless and tasteless. The sp. w. of the solid is from 1.96 to 2.07. It melts at about  $114^\circ \text{C}$ . to an amber-colored liquid. If the fusion is effected at not over  $120^\circ$  in a ladle or crucible, the contents allowed to cool slowly until a crust is formed on the surface, the crust perforated by a hot iron at two opposite points, and the still liquid portion of the sulphur poured off through one of the perforations, the vessel will be found to contain well developed long prismatic crystals of sulphur which are at first transparent but afterwards become opaque owing to the fact that each needle-like prism breaks up into very small rhombic octohedrons.

Large rhombic octohedral crystals can be obtained by the evaporation of a solution of sulphur in carbon disulphide.

When sulphur is heated beyond  $150^{\circ}$  C. the liquefied element becomes darker and thickens; near  $200^{\circ}$  it is nearly black and so tough that it can scarcely be poured; at a still higher temperature it becomes somewhat thinner again, so that it runs; if then poured into water and cooled it forms a soft, tough, yellowish-brown solid which can be drawn into threads. This plastic amorphous sulphur is insoluble in carbon disulphide. But in a few hours it loses its plasticity and gradually becomes hard, brittle, and again soluble in carbon disulphide, not, however, without leaving an undissolved residue of brown powder which must be fused in order to regain the normal properties of sulphur.

Sulphur boils at about  $446^{\circ}$  C., forming a dark-brownish vapor which at  $480^{\circ}$  acquires a density of 95.85, indicating that the molecule is at that temperature hexatomic. But sulphur does not exhibit a fixed density below  $1,000^{\circ}$  C., and at  $1040^{\circ}$  its vapor density indicates that it then consists of diatomic molecules.

In commerce sulphur occurs in three forms: 1, "*brimstone*," or "roll-sulphur," which is an impure sulphur molded into cylindrical sticks which are about one inch or more in diameter, pale yellow, crystalline in the fracture, and have a distinct, peculiar, though faint, odor, increased by friction; 2, *sublimed sulphur*, or "flowers of sulphur," which is a fine, largely crystalline, light yellow powder having a very slight characteristic odor and a slightly acid taste; and 3, *precipitated sulphur*, which is a very fine amorphous, pale greenish-yellow, odorless and tasteless powder.

Sulphur, when heated, first melts and then vaporizes without residue, if pure. When ignited it burns to sulphur dioxide, which is at once recognized by its characteristic pungent odor and its irritating effect upon the respiratory organs.

Sulphur is insoluble in water and in alcohol; but it is readily soluble in benzin, benzol, oil of turpentine and several other oils, ether and chloroform. Precipitated sulphur dissolves completely as well as readily in carbon disulphide; but sublimed sulphur is only partially soluble in that solvent.

Sulphur dissolves in large proportions when boiled in aqueous solutions of the alkaline hydroxides, such as those of potassium, sodium, barium and calcium, forming freely soluble sulphides,

mono-thiosulphates and tetrathiosulphates. These solutions are yellowish-red and have a strong odor similar to that of hydrogen sulphide.

**630. Chemical properties.** Sulphur of negative polarity is perfectly analogous to oxygen. Its polarity-value is  $-2$ , and it forms compounds of a structure exactly similar to that of the corresponding oxygen compounds.

But sulphur is positive toward oxygen and the halogens, and, when in combination with them, exhibits polarity-values of  $+2$ ,  $+4$  and  $+6$ . When two or more sulphur atoms are directly united to each other one or more of these atoms must necessarily have a polarity-value of  $0$ , as is the case with oxygen atoms thus connected with each other. In hyposulphites the sulphur atom has a polarity-value of  $+2$ ; in sulphites of  $+4$ ; in sulphates  $+6$ . In monothiosulphates, as in the ordinary sodium thiosulphate, the acidic sulphur atom has a polarity-value of  $+6$  and the negative sulphur atom (which takes the place of an oxygen atom) has a value of  $-2$ . In the so-called polysulphides of the alkali metals we also have both acidic sulphur and negative sulphur. In  $K_2S_8$ , which is really a sulphur salt instead of a sulphide, the acidic sulphur atom has a polarity-value of  $+2$ , while the two negative sulphur atoms have the polarity-value of  $-2$ , for  $K_2S_8$  is  $K_2SS_2$ , corresponding to  $K_2SO_2$ . In  $K_2S_5$  we recognize  $K_2SS_4$  corresponding to  $K_2SO_4$ .

At ordinary temperatures sulphur does not display marked chemical energy, although when in intimate contact, in a moist condition, with various metals or their compounds, it may attack them to some extent. But at high temperatures sulphur exhibits very great energy and can combine with nearly all other elements.

**631. Compounds.** The analogy between the compounds formed by oxygen and those formed by *negative* sulphur is shown in the following exhibit:

<i>Oxygen Compounds.</i>	<i>Sulphur Compounds.</i>
$H_2O$ , or $HOH$	$H_2S$ , or $HSH$
$H_2O_2$ , or $HOOH$	$H_2S_2$ , or $HSSH$
$FeO$	$FeS$
$CuO$	$CuS$
$HgO$	$HgS$
$CO_2$	$CS_2$

<i>Oxygen Compounds.</i>	<i>Sulphur Compounds.</i>
$\text{Sb}_2\text{O}_3$	$\text{Sb}_2\text{S}_3$
$\text{P}_2\text{O}_3$	$\text{P}_2\text{S}_3$
$\text{P}_2\text{O}_5$	$\text{P}_2\text{S}_5$
$\text{NaOH}$	$\text{NaSH}$
$\text{KOH}$	$\text{KSH}$
$\text{H}_4\text{NOH}$	$\text{H}_4\text{NSH}$
$\text{Na}_2\text{CO}_3$	$\text{Na}_2\text{CS}_3$
$\text{Ca}(\text{OH})_2$	$\text{Ca}(\text{SH})_2$
$\text{Ca}_3(\text{AsO}_4)_2$	$\text{Ca}_3(\text{AsS}_4)_2$
$\text{Na}_3\text{SbO}_3$	$\text{Na}_3\text{SbS}_3$
$\text{Na}_3\text{SbO}_4$	$\text{Na}_3\text{SbS}_4$
$\text{Na}_2\text{SO}_4$	$\text{Na}_2\text{SS}_4$

*Hydrogen sulphide*,  $\text{HSH}$ , or  $\text{H}_2\text{S}$ , is a colorless gas having a strong odor, very suggestive of decayed eggs. It is inflammable. It is soluble in water, a saturated solution at  $15^\circ \text{C}$ . containing about 3.25 volumes of the gas dissolved in 1 volume of water. Such a solution is extensively employed as a reagent in the laboratories. Hydrogen sulphide is a reducing agent.

The gas is commonly prepared by the action of dilute sulphuric acid upon ferrous sulphide:



*Sulphur dichloride*,  $\text{SCl}_2$ , and tetrachloride,  $\text{SCl}_4$ , are volatile, unstable liquids;  $\text{S}_2\text{Cl}_2$  also exists.

With *bromine* sulphur forms  $\text{S}_2\text{Br}_2$ .

Two *iodides of sulphur* are known, namely,  $\text{S}_2\text{I}_2$  and  $\text{SI}_6$ . The compound  $\text{S}_2\text{I}_2$  is officinal.

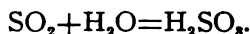
The constitution of  $\text{S}_2\text{Cl}_2$ ,  $\text{S}_2\text{Br}_2$  and  $\text{S}_2\text{I}_2$  must be either such as shown in  $\text{Cl}-\text{S}-\text{S}-\text{Cl}$ , or in  $\text{SSCl}_2$ . In the former one sulphur atom has a polarity-value of 0, while the other has a polarity-value of +2; in the other we have one sulphur atom with a polarity-value of +4, while the second sulphur atom is negative, the molecule being analogous with  $\text{SOCl}_2$ .

The *oxides of sulphur* are sulphur dioxide;  $\text{SO}_2$ , and sulphur trioxide,  $\text{SO}_3$ .

Sulphur dioxide is a gas; the trioxide, when pure, is a liquid.

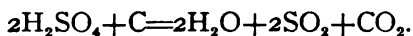
*Sulphur dioxide* is formed when sulphur burns. It has a pungent, suffocating odor, and is very irritant and poisonous when inhaled. Its bleaching power is great. It acts as a powerful re-

ducing agent. When dissolved in water it forms sulphurous acid which has the odor and some other characteristic properties of the gas:

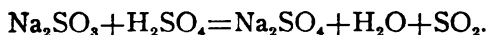


Oxidizing agents change sulphurous acid to sulphuric acid.

Sulphur dioxide may be prepared not only by the combustion of sulphur but also by the reduction of sulphuric acid effected by heating that acid with charcoal.



Sulphur dioxide is also produced by the decomposition of sulphites with some stronger acid:



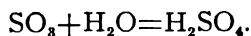
It is formed, further, when copper or mercury is heated with sulphuric acid:



*Sulphur trioxide* is produced by strongly heating certain metallic sulphates. Ferrous sulphate is employed for the manufacture of "fuming sulphuric acid," called "Nordhausen sulphuric acid, which is a mixture of sulphuric acid and sulphur trioxide, or perhaps a definite chemical compound which is called pyrosulphuric acid,  $\text{H}_2\text{S}_2\text{O}_7 = \text{H}_2\text{SO}_4 + \text{SO}_3$ . The trioxide can be separated from this fuming sulphuric acid by heat.

Pure sulphur trioxide is a colorless liquid at ordinary temperatures but a white crystalline solid below  $15^\circ \text{C}$ .; it is not corrosive if quite dry. But the ordinary sulphur trioxide which is a crystalline solid containing some water, is strongly acid and extremely corrosive.

When sulphur trioxide is put in water a violent chemical reaction ensues, accompanied by a hissing noise produced by the rapid formation of water vapor on account of the great heat generated by the reaction, sulphuric acid being formed:



The important *acids* in which sulphur performs the acidic function are:

Hyposulphurous acid,  $\text{H}_2\text{SO}_2$ , or  $(\text{HO})_2\text{S}$ .

Hypothiosulphurous acid,  $\text{H}_2\text{SS}_2$ , or  $(\text{HS})_2\text{S}$ .

Sulphurous acid,  $\text{H}_2\text{SO}_3$ , or  $(\text{HO})_2\text{SO}$ .

Sulphuric acid,  $\text{H}_2\text{SO}_4$ , or  $(\text{HO})_2\text{SO}_2$ .

Thiosulphuric acid,  $\text{H}_2\text{SO}_3\text{S}$ , or  $(\text{HO})_2\text{SOS}$  or  ~~$\text{HOSOSO}_2$~~   $\text{HOHSO}_2$ .

Tetrathiosulphuric acid,  $\text{H}_2\text{SS}_4$ , or  $(\text{HS})_2\text{SS}_2$ .

Tetrathionic acid,  $\text{H}_2\text{S}_4\text{O}_6$ , or  $(\text{HO})_2\text{S}_4\text{O}_4$ .

The three last named are known only or chiefly through their salts.

*Volatile sulphur compounds* generally have a strong odor, as exemplified by  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{CS}_2$ , and by the sulphurated volatile oils of mustard, garlic, asafetida, etc.

**632. The Official Sulphides** include hydrogen sulphide, as a reagent, ferrous sulphide as one of the materials used in the preparation of hydrogen sulphide, carbon disulphide, and:

$\text{CaS}$ , Calcium sulphide, contained in "sulphurated lime" together with calcium ~~tetrathio~~ sulphate. Yellow, hygroscopic. Freely soluble. 1

$\text{K}_2\text{S}$ , Potassium sulphide, contained in "sulphurated potassa" together with potassium hypothiosulphite. Yellow. Freely soluble.

$\text{HgS}$ , Mercuric sulphide. Red when crystalline; black when amorphous. Insoluble.

$\text{Sb}_2\text{S}_3$ , Antimonous sulphide. Black when crystalline; red when amorphous. Insoluble.

$\text{Sb}_2\text{S}_5$ , Antimonic sulphide. Red, amorphous powder. Insoluble.

The "sulphurated potassa," potassa sulphurata, of the Pharmacopœa, consists chiefly of  $\text{K}_2\text{SS}_2$  and is liver-colored, and the "sulphurated lime," calx sulphurata, is mainly composed of  ~~$\text{CaS}_2$~~   $\text{CaS}$ .

The only water-soluble sulphides are those of hydrogen; the alkali metals, and the metals of the alkaline earths.

Many metallic sulphides occur in nature.

In some cases the crystallized sulphide is of a different color from that of the amorphous sulphide of the same metal.

**633. Methods of preparation** of the sulphides.

Hydrogen does not combine with sulphur except when both are in the nascent state, and hence hydrogen sulphide must be

prepared by decomposing some other sulphide by an acid; ferrous sulphide and dilute sulphuric acid are generally used.

The sulphides of the alkali metals and alkaline earth metals may be produced, together with sulphur salts, by heating sulphur with their hydroxides or carbonates, or by boiling the solutions of the hydroxides with sulphur, or by reducing the sulphates by ignition with charcoal or some other form of carbon.

The sulphides of other metals, being insoluble in water, are prepared by precipitation; but many of them may be made by fusing the metal with sulphur.

**634. Reactions of Sulphides.** When metallic sulphides are treated with dilute sulphuric acid or with other acids, hydrogen sulphide is generally given off which is readily recognized by its offensive odor. But the sulphides of arsenic and antimony which correspond in chemical behavior to the acid-forming oxides are soluble in solutions of the alkalis and insoluble in acids which do not decompose them. Sulphides corresponding to the basic oxides are decomposed by the acids and insoluble in alkali solutions. Sulphides corresponding to the indifferent oxides are insoluble in both acids and alkalis.

**635. Sulphuric Acid.** The ordinary sulphuric acid represented by most of the metallic sulphates is  $\text{H}_2\text{SO}_4$ , a di-meta-acid. Concentrated sulphuric acid consists chiefly of  $\text{H}_2\text{SO}_4$ . But when sulphuric acid is diluted with water it probably contains mono-meta-sulphuric acid, or normal sulphuric acid, or both.

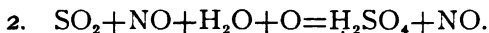
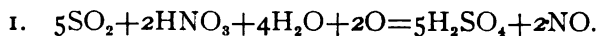
Sulphuric acid is *produced* as follows: Sulphur dioxide,  $\text{SO}_2$ , formed by burning sulphur or by roasting iron pyrites, is brought together with nitric acid and water, in the state of vapor, in lead lined chambers. Air is also introduced. The nitrogen of the nitric acid acts as a carrier of oxygen from the air to the sulphur of the sulphur dioxide. The reactions believed to occur are:

1.  $\text{SO}_2 + \text{HNO}_3 = \text{HONO}_2\text{SO}_2$ .
2.  $2\text{HONO}_2\text{SO}_2 + \text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 + \text{NO} + \text{NO}_2$ .
3.  $2\text{SO}_2 + \text{NO} + \text{NO}_2 + 2\text{O} + \text{H}_2\text{O} = 2\text{HONO}_2\text{SO}_2$ .
4.  $2\text{HONO}_2\text{SO}_2 + \text{SO}_2 + 2\text{H}_2\text{O} = 3\text{H}_2\text{SO}_4 + 2\text{NO}$ .

The compound  $\text{HONO}_2\text{SO}_2$  is called nitroso-sulphuric acid. The NO very readily takes up more oxygen from the air intro-

duced, forming nitroso-sulphuric acid with sulphur dioxide and water (injected as steam), and the nitroso-sulphuric acid, in turn, reacts with more water to form sulphuric acid and the nitrogen oxides, so that the process is a continuous one which theoretically requires no additional nitric acid. But as the nitrogen of the air introduced in the series of chambers in which these reactions occur accumulates, and must be from time to time removed, a loss of the nitrogen oxides is unavoidably sustained at the same time, so that more nitric acid must be added as required to keep up the oxidation of the  $\text{SO}_2$ .

If the intermediate reactions be left out of consideration the whole process may be summarized in the equations:



The second equation just given contains the NO in both of its members to indicate that it is a necessary factor and serves as a carrier of oxygen, for without the mediation of the NO the  $\text{SO}_2$  can not form sulphuric acid with water and oxygen.

**636.** Sulphuric acid is under ordinary conditions the most powerful of all acids, decomposing the salts of other acids. The energy with which it reacts with other substances, and hence its extremely destructive properties, must be the resultant of the unequal chemical energy of hydrogen and the compound radical  $\text{SO}_4$ . The sulphates of powerful positive elements such as potassium, sodium, barium and calcium are very stable molecules at ordinary temperatures, but hydrogen sulphate is easily decomposed by many of the metals and by most of the metallic oxides, hydroxides, carbonates and various other metallic compounds, the hydrogen of the acid being replaced by metal.

Normal sulphuric acid,  $(\text{HO})_2\text{S}$ , does not seem to form any salts; water is split off from it when it is neutralized or saturated so that mono-meta-sulphates or di-meta-sulphates are formed. Among the common sulphates those of magnesium and zinc, and ferrous and manganous sulphate are mono-meta-sulphates, or the salts of  $\text{H}_4\text{SO}_5$ .

**637. Sulphates.** The metallic sulphates are *generally water-soluble*. But the sulphates of barium, strontium and lead are *in-*

*soluble*, and calcium sulphate is *very sparingly soluble*. Mercuric sulphate is decomposed by water.

The *official sulphates* are all water-soluble, except those of calcium and mercury. They are:

$\text{H}_2\text{SO}_4$ , Sulphuric acid; acidum sulphuricum. Colorless liquid.

$\text{K}_2\text{SO}_4$ , Potassium sulphate; potassii sulphas. White or colorless, crystalline. Soluble.

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , Sodium sulphate; sodii sulphas. Colorless, crystalline. Readily soluble.

$(\text{H}_4\text{N})_2\text{SO}_4$ , Ammonium sulphate; ammonii sulphas. Colorless, crystalline. Readily soluble.

$\text{MgH}_2\text{SO}_5 \cdot 6\text{H}_2\text{O}$ , Magnesium sulphate; magnesii sulphas. Colorless or white, crystalline. Soluble.

$\text{ZnH}_2\text{SO}_5 \cdot 6\text{H}_2\text{O}$ , Zinc sulphate; zinci sulphas. White or colorless, crystalline. Soluble.

$\text{FeH}_2\text{SO}_5 \cdot 6\text{H}_2\text{O}$ , Ferrous sulphate; ferri sulphas. Pale bluish-green; crystalline. Soluble.

$\text{FeH}_2\text{SO}_5$ , Dried ferrous sulphate; ferri sulphas exsiccatus. Nearly white powder. Slowly soluble.

$\text{MnH}_2\text{SO}_5 \cdot 6\text{H}_2\text{O}$ , Manganous sulphate; mangani sulphas. Pale red, crystalline. Soluble.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , Cupric sulphate; cupri sulphas. Blue, crystalline. Soluble.

$\text{HgSO}_4$ , Mercuric sulphate; hydrargyri sulphas. White; crystalline. Decomposed by water.

$\text{Hg}(\text{HgO})_2\text{SO}_4$ , Yellow basic mercuric sulphate; hydrargyri subsulphas flavus. Lemon-yellow, crystalline powder. Insoluble.

$\text{Al}_2(\text{SO}_4)_3$ , Aluminum sulphate; alumini sulphas. White, crystalline. Readily soluble.

$\text{AlK}(\text{SO}_4)_2$ , Dried alum; alumen exsiccatum. White powder or pieces. Slowly soluble.

$\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , Alum; alumen. Colorless crystals. Readily soluble.

$\text{AlH}_4\text{N}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , Ammonia alum; alumini et ammonii sulphas. Colorless crystals. Readily soluble.

$\text{FeH}_4\text{N}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , Iron alum; ferri et ammonii sulphas. Purple or pink, crystalline. Readily soluble.

$\text{Fe}_2(\text{SO}_4)_3$ , Ferric sulphate; ferri tersulphas. Pale yellow, amorphous. Freely soluble, yielding a red-brown solution.

$\text{Fe}_4\text{O}(\text{SO}_4)_6$ , Basic ferric sulphate; ferri subsulphas. Pale yellow, amorphous, extremely freely soluble, hygroscopic, yielding a red-brown solution.

Solutions of normal ferric sulphate and of basic ferric sulphate are also officinal.

**638.** Metallic sulphates which are soluble in water or in sulphuric acid may be *produced* by saturating the acid with the metal or its oxide, hydroxide, carbonate (or sulphide).

Insoluble metallic sulphates are produced from soluble sulphates by precipitation.

Mercuric sulphate is prepared by heating mercury with sulphuric acid, or with sulphuric acid and nitric acid. Mercurous sulphate is prepared by triturating the mercuric sulphate with as much mercury as it already contains.

**639. Reactions of Sulphates.** Sulphuric acid and other sulphates are identified or detected by barium chloride or barium nitrate solution, for barium sulphate is quite insoluble not only in water but in nitric acid. Hence a white precipitate is formed on the addition of a solution of any water-soluble barium salt to a solution of any sulphate and this precipitate is not dissolved on addition of nitric acid.

Some sulphates when strongly heated remain unaltered, but the sulphates of the heavy metals are decomposed, giving off  $\text{SO}_2$  or  $\text{SO}_3$ .

When sulphates are strongly heated on charcoal with sodium carbonate they are reduced and sodium sulphide is formed.

**640. Thiosulphates.** The only officinal thiosulphate is that of sodium, a colorless crystalline readily soluble salt, having the structure  $\text{Na}_2\text{SO}_3\text{S}$ . It is looked upon as differing from ordinary sodium sulphate,  $\text{Na}_2\text{SO}_4$ , only in that it contains one negative sulphur atom in the place of one of the oxygen atoms of that salt. It is accordingly a mono-thiosulphate. This salt is commonly called "hyposulphite of sodium," and even Pharmacopœias still retain that title for it, although sodium hyposulphite,  $\text{Na}_2\text{SO}_3$ , exists.

The so-called potassium trisulphide,  $K_2S_3$ , is potassium hypothyiosulphite,  $(KS)_2S$ .

Sodium tetrathiosulphate,  $Na_2SS_4$ , and calcium tetrathiosulphate,  $CaSS_4$ , are freely water-soluble yellow salts commonly referred to as pentasulphides— $Na_2S_5$  and  $CaS_5$ .

**641. Sulphites.** Sulphurous acid,  $H_2SO_3$ , a mono-meta-acid, is formed when  $SO_2$  is dissolved in water. It is a comparatively weak acid and its salts are decomposed by other acids,  $SO_2$  being given off, by which these salts may be *identified*.

The sulphites of potassium and sodium are readily water-soluble; other metallic sulphites are rather sparingly soluble.

Sulphurous acid and  $SO_2$  as well as the sulphites are reducing agents, bleaching agents, and are frequently used as preservatives of organic substances, such as fruit juices, etc.

Sulphites may be *produced* by the action of sulphurous acid, or of  $SO_2$ , upon hydroxides, oxides, and carbonates, in water.

The *officinal sulphites* are:

$H_2SO_3$ , Sulphurous acid; acidum sulphurosum. Used in solution containing 12.8 per cent of  $H_2SO_3$ , representing 6.4 per cent of  $SO_2$ . Colorless liquid.

$Na_2SO_3 \cdot 7H_2O$ , Sodium sulphite; sodii sulphis. White salt. Soluble.

$CaSO_3 \cdot 2H_2O$ , Calcium sulphite; calcii sulphis. White salt. Soluble.

$MgSO_3 \cdot 6H_2O$ , Magnesium sulphite; magnesii sulphis. White salt. Soluble.

## CHAPTER XXXVI.

### NITROGEN.

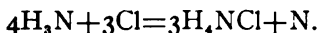
Symbol, N. At. w., 14.

**642. Occurrence.** The atmosphere consists of a mixture composed almost entirely of the two gases nitrogen and oxygen. About four-fifths of the total weight of the air is nitrogen.

Nitrogen also occurs in the form of sodium nitrate in the salt-petre deposits of South America.

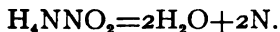
**643. Preparation.** The oxygen may be removed from the air by the combustion of phosphorus in it. When air is passed over heated copper the metal is oxidized and the nitrogen thus freed from the oxygen.

Nitrogen can also be obtained from ammonia by conducting a current of chlorine into ammonia water:



But the preparation of nitrogen by this process, although easy and convenient, is attended with great danger unless the current of chlorine is cut off before all of the ammonia has been decomposed. As long as any ammonia remains there is no danger; but when the chlorine can no longer form ammonium chloride the fearfully explosive nitrogen chloride,  $\text{NCl}_3$ , will instead be formed.

Nitrogen can also be prepared by boiling a strong solution of ammonium nitrite:



**644. Description.** Nitrogen is a colorless, odorless, tasteless, non-combustible gas. Under a pressure of 35 atmospheres at or below  $146^\circ$  it is condensed to a liquid.

One cubic-decimeter of pure nitrogen at  $0^\circ\text{C}$ ., bar. 760 MM., weighs about 1.26 Gm.

Nitrogen is practically insoluble in water.

**645. Chemical properties.** Nitrogen with negative polarity is a triad; with positive polarity it may be either a monad, dyad,

triad, tetrad or pentad. A nitrogen atom may have both positive and negative units of combining value, as is shown in  $\text{H}_4\text{NCl}$ , and in  $\text{H}_4\text{NOH}$ , in both of which the nitrogen atom has four negative and one positive bond and, therefore, a polarity-value of  $-3$ .

Unusual means are necessary to compel nitrogen to enter into chemical union with other elements, and the compounds formed by it are generally easily decomposed again, frequently with explosive violence. The extremely indifferent chemical energy of nitrogen must be supported by such aids as the *status nascens*, predisposing affinity, and other means in order to cause it to enter into chemical combination.

The polyvalence and indifferent chemical energy of nitrogen account for the ruling characteristics of its most important compounds, which are singularly interesting. The complex constitution and instability of the nitrogen compounds which serve as the materials for the construction of certain animal tissues are significant.

Our most powerful *explosives*, like nitroglycerin, dynamite, gun cotton, etc., are nitrogen compounds.

With the halogens and with sulphur, nitrogen forms extremely explosive compounds, the formation of which must be carefully avoided in laboratory operations.

The fearfully poisonous *toxines* formed by the decomposition of animal matter, and toxalbumens, the formation of which is caused by bacteria, are also nitrogen compounds. So are the *alkaloids*. The extremely poisonous cyanogen compounds further emphasize the dangerous character of many of the nitrogen compounds.

Nitric acids and the nitrates are very effective oxidizing agents because of the high polarity-value of their nitrogen and the facility with which they undergo dissociation and reduction.

Among the remarkable compound radicals formed by nitrogen are ammonium,  $\text{H}_4\text{N}$ ; nitrosyl,  $\text{NO}$ ; nitryl,  $\text{NO}_2$ ; cyanogen,  $\text{CN}$ ; amidogen,  $\text{NH}_2$ ; imidogen,  $\text{NH}$ .

**646. Compounds.** *Hydrogen* forms the nitride *ammonia*,  $\text{H}_3\text{N}$ . This is a colorless gas, having an excessively pungent, stifling odor. The inhalation of this gas in large quantities or undiluted is dangerous and may prove fatal. Ammonia can be liquefied under a pressure of seven atmospheres at  $15^\circ \text{C}$ . It is readily soluble in water, with which it forms ammonium hydroxide,

$\text{H}_4\text{NOH}$ . At  $0^\circ \text{C}$ . 1 volume of water dissolves 1050 volumes of ammonia gas, and at  $15^\circ \text{C}$ . about 730 volumes.

Ammonia has strongly alkaline properties and forms salts with the acids. Ammonia solutions are indispensable in chemical laboratories.

Five *oxides* of nitrogen are recognized, namely:  $\text{N}_2\text{O}$ ,  $\text{NO}$  (formerly written  $\text{N}_2\text{O}_2$ ),  $\text{N}_2\text{O}_3$ ,  $\text{NO}_2$ , and  $\text{N}_2\text{O}_5$ . But  $\text{N}_2\text{O}_4$  also exists.

The *trioxide*,  $\text{N}_2\text{O}_3$ , is described as a blue liquid. The *peroxide*,  $\text{NO}_2$ , or  $\text{N}_2\text{O}_4$ , in its behavior toward bases, acts as if it were a mixture of  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_5$ , forming both nitrites and nitrates; at temperatures above  $150^\circ$   $\text{NO}_2$  exists as a red vapor, but this condenses at lower temperatures into an orange colored liquid of the composition  $\text{N}_2\text{O}_4$ . To avoid confusion the  $\text{NO}_2$  should be called nitrogen peroxide and the  $\text{N}_2\text{O}_4$  nitrogen tetroxide.

The separate existence of  $\text{N}_2\text{O}_3$  seems to be problematic.

Nitric *pentoxide*,  $\text{N}_2\text{O}_5$ , is a white solid which forms nitric acid with water:  $\text{N}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{HNO}_3$ .

The *nitric oxide*,  $\text{NO}$ , is nearly always produced when nitric acid is acted upon by a metal; it is a colorless gas, but when formed in the air it immediately takes up more oxygen and is converted into  $\text{NO}_2$  or  $\text{N}_2\text{O}_4$ , or both (according to the temperature), constituting the well known "red nitrous vapors."

$\text{N}_2\text{O}$  is commonly called "nitrous oxide gas," or "laughing gas." It is colorless. It may be made by heating dry ammonium nitrate:  $\text{H}_4\text{NNO}_3 = 2\text{H}_2\text{O} + \text{N}_2\text{O}$ . When inhaled this gas temporarily sustains respiration, but causes more or less hysterical excitement, very brief anæsthesia, and, when impure or carelessly administered, or when inhaled by persons whose heart and lungs are not in a sound, normal condition, it may cause death. It is employed by dentists to render patients insensible to pain in the extraction of teeth.

The important *acids* formed by nitrogen are: Nitrous acid,  $\text{HNO}_2$ ; and nitric acid,  $\text{HNO}_3$ .

**647. Nitrates.** Nitric acid,  $\text{HNO}_3$ , is a di-meta-acid and one of the most powerful acids known. It is extremely corrosive and destructive. It is made by distilling nitrates with sulphuric acid.

Nitric acid and other nitrates are unstable, at least at high temperatures, and are used as oxidizing agents on that account and

because of the high polarity-value of the acidic element which is readily reduced.

All metallic nitrates are water-soluble except those of mercury and bismuth, which are decomposed by any considerable quantity of water, but which are soluble in nitric acid. The metallic nitrates are, therefore, generally *produced* by dissolving the metals in nitric acid or by saturating that acid with their oxides, hydroxides or carbonates.

**648.** The **official nitrates** include:

$\text{HNO}_3$ , Nitric acid; acidum nitricum. This is still sometimes called "aqua fortis." Colorless liquid.

$\text{KNO}_3$ , Potassium nitrate; potassii nitras. Commonly called "saltpetre," and "nitre." White, crystalline. Soluble.

$\text{NaNO}_3$ , Sodium nitrate; sodii nitras. White, crystalline. Soluble.

$\text{H}_4\text{NNO}_3$ , Ammonium nitrate; ammonii nitras. White or colorless, crystalline. Soluble.

$\text{AgNO}_3$ , Silver nitrate; argenti nitras. This, when fused and molded into pencils, is called "lunar caustic." White or colorless, crystalline. Soluble.

$\text{Ba}(\text{NO}_3)_2$ , Barium nitrate; barii nitras. White or colorless, crystalline. Soluble.

$\text{Sr}(\text{NO}_3)_2$ , Strontium nitrate; strontii nitras. White or colorless, crystalline. Soluble.

$\text{Pb}(\text{NO}_3)_2$ , Lead nitrate; plumbi nitras. White or colorless, crystalline. Soluble.

$\text{Cu}(\text{NO}_3)_2$ , Cupric nitrate; cupri nitras. Blue, crystalline. Soluble.

$\text{HgNO}_3$ , Mercurous nitrate; hydrargyri mononitras. White, crystalline. Decomposed by water.

$\text{Hg}(\text{NO}_3)_2$ , Mercuric nitrate; hydrargyri dinitras. This is referred to in the title of the official solution as "Hydrargyri Nitras." White, crystalline. Decomposed by water.

$\text{Bi}(\text{NO}_3)_3$ , Normal bismuth nitrate; bismuthi trinitras. Colorless, crystalline. Decomposed by water.

$\text{OBiNO}_3$ , Bismuthyl nitrate; bismuthyl nitras. Called, officially, "subnitrate of bismuth;" bismuthi subnitras. White powder. Insoluble.

$\text{Fe}(\text{NO}_3)_3$ , Ferric nitrate; ferri nitras. Of this the Pharmacopœia contains a solution. Yellow; solution reddish.

**649. Reactions of Nitrates.** The nitrates give off red vapors of  $\text{NO}_2$  (or  $\text{N}_2\text{O}_4$ ) when heated in a test-tube with copper filings and sulphuric acid.

They instantly decompose when placed on charcoal heated to redness, the carbon burning with great brilliancy, owing to the nascent oxygen liberated from the dissociated nitrates.

When a liquid containing a minute amount of nitric acid or a nitrate is mixed with an equal volume of undiluted sulphuric acid, the mixture allowed to cool, and a crystal of ferrous sulphate is added, a brownish-black color appears around the crystal.

**650. Nitrites.** Nitrous acid is  $\text{HNO}_2$ , a mono-meta-acid. It is frequently contained in small quantities in strong nitric acid, but it is not known in its pure state. Nitrites are, however, well known.

Sodium nitrite is the only officinal metallic nitrite.

The nitrites give off red nitrous vapors on the addition of dilute sulphuric acid.

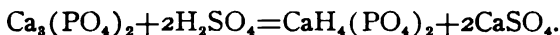
## CHAPTER XXXVII.

### PHOSPHORUS.

Symbol, P. At.w. 31.

**651. Occurrence and preparation.** Phosphorus occurs mainly in the form of calcium phosphate in the mineral *apatite* and in bones. The phosphorus compounds of bones and other animal substances are formed from the phosphorus compounds taken from the soil by plants.

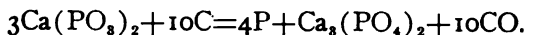
Phosphorus is made from bone phosphate, called "calcined bone," or "bone-ash," which is first treated with strong sulphuric acid to form acid calcium phosphate:



The acid calcium phosphate is leached out with water from the calcium sulphate. The solution of acid phosphate is boiled down to the consistence of syrup and mixed with charcoal. The pasty mixture is dried and then heated in an earthenware retort, the neck of which dips into water. The first effect of the heat is the transformation of the acid calcium orthophosphate into meta-phosphate:



Next, at a higher temperature, the meta-phosphate is decomposed by the carbon:



The residuary calcium phosphate is used again. Phosphorus distills over into the water. It is purified by redistillation and by straining it through wash-leather under warm water. Finally it is fused and molded into sticks.

The intense heat obtained by means of the electric arc in what is called the electric furnace is now utilized in the production of phosphorus from phosphates by reduction with coke or charcoal.

**652. Description.** Perfectly pure *waxy phosphorus* is a soft,

white, semi-translucent solid of peculiar odor and taste. It is of crystalline structure; luminous in the dark; sp. w. 1.830 at 10° C.; melts at 44° C., boils at 250°.

Common waxy phosphorus is more or less yellowish, and contains arsenic and sulphur.

Exposed to the air phosphorus emits white fumes. On longer exposure it ignites spontaneously. It must, therefore, be kept under water, and it is best to put it in strong, glass-stoppered bottles, which should be kept in a cool, secure place. The *poisonous properties* of Phosphorus are such that *it should not be tasted*, and it is so *inflammable* that it must be handled with the greatest care.

Phosphorus may be converted into a coarse granular powder by melting it in a bottle containing a saturated solution of sodium chloride, the bottle and contents being heated by means of hot water, and then shaking until cool, after which the solution of sodium chloride may be poured off and replaced by pure water after sufficiently washing the granulated phosphorus. The bottle used to granulate the phosphorus should be only about one-half or two-thirds filled with the solution of sodium chloride to permit effective shaking of the contents.

Phosphorus is practically insoluble in water, but imparts to it its characteristic odor and taste. It is soluble in 350 parts of *absolute* alcohol at 15° C., in 80 parts of absolute ether, and in about 50 parts of any fixed oil. It is very freely soluble in chloroform and in carbon disulphide. The solution of phosphorus in carbon disulphide is extremely inflammable.

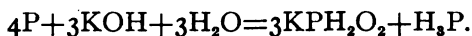
*Red phosphorus* is another allotropic form of the element. The waxy phosphorus, or ordinary form, is converted into the red modification by heating it in a closed vessel to about 300° C. The red phosphorus is an amorphous dark-red powder of about 2.1 sp. w. The igniting point of red phosphorus is about 444°, so that it is not dangerous to handle, nor is this variety of phosphorus poisonous. It is not oxidizable in the air at ordinary temperatures, nor luminous in the dark. It is infusible, and is insoluble in carbon disulphide.

**653. Chemical properties.** Waxy phosphorus possesses such strong affinity for oxygen that it ignites spontaneously when exposed to the air, and burns fiercely, being oxidized to phosphorus pentoxide.

Negative phosphorus is, like nitrogen, a triad; but positive phosphorus may have a polarity-value of either +1, or +3 or +5.

The density of its vapor indicates that the molecule of phosphorus is tetratomic.

**654. Compounds.** *Hydrogen phosphide*, or phosphorus, is an inflammable poisonous gas having a strong garlicky odor. It is formed when phosphorus is boiled with KOH, NaOH, or  $\text{Ca}(\text{OH})_2$ , in water. The reaction is:



A small quantity of another hydrogen phosphide,  $\text{H}_4\text{P}_2$ , is concurrently formed, and this renders the gas *spontaneously* inflammable. When  $\text{H}_3\text{P}$  burns it forms  $\text{P}_2\text{O}_5$  and water, and the series of smoke-like white rings which appear consist of the pentoxide.

Phosphine is not alkaline like  $\text{H}_3\text{N}$ , but with hydriodic acid it forms phosphonium iodide,  $\text{H}_4\text{PI}$ . Other compounds of phosphonium,  $\text{H}_4\text{P}$ , are also known.

The *oxides* of phosphorus are  $\text{P}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ . The trioxide is a white powder forming phosphorous acid with water. The pentoxide is a white, snow-like solid, which forms phosphoric acid with water.

The compounds formed by phosphorus with the *halogens* are of considerable importance in organic chemistry.

The *acids* of phosphorus are:

Hypophosphorous acid,  $\text{HPH}_2\text{O}_2$ .

Phosphorous acid,  $\text{H}_3\text{PO}_3$ .

Orthophosphoric acid,  $\text{H}_3\text{PO}_4$ .

Metaphosphoric acid,  $\text{HPO}_3$ .

Pyrophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_7$ .

**655. The phosphates.** Common phosphoric acid is  $\text{H}_3\text{PO}_4$ , called "orthophosphoric acid." As may be seen from its molecular formula it is a mono-meta-acid. It is a strong acid and its salts are very stable because it is not volatile.

Phosphoric acid is *produced* in various ways. For experimental purposes it may be made from phosphorus pentoxide and water. If an impure acid satisfies the requirements it can be obtained, containing a considerable quantity of acid calcium phos-

phate, by decomposing bone ash (calcium phosphate) with sulphuric acid. But pure phosphoric acid for pharmaceutical purposes is produced from phosphorus by methods which are fully described in Vol. II, where the properties of the product are also discussed.

*Solubility.*—The only *water-soluble* phosphates are those of potassium, sodium, and ammonium. But calcium phosphate, phosphate of iron, and some other metallic phosphates are soluble in phosphoric acid. It must be remembered, however, that metallic orthophosphates soluble in orthophosphoric acid may be insoluble in metaphosphoric acid, and that metaphosphates and pyrophosphates soluble in metaphosphoric acid may be insoluble in orthophosphoric acid; this is the case with the iron phosphates. Ferric phosphate, ferric pyrophosphate, and ferric hypophosphite are soluble in strong solutions of citrate of potassium, sodium, or ammonium.

*Preparation.*—The water-soluble phosphates can, of course, be made from phosphoric acid by neutralizing the acid with the alkali carbonates; but they are more cheaply and very satisfactorily made by adding the alkali carbonates to a solution of acid calcium phosphate. Insoluble phosphates are produced by precipitation, as insoluble salts usually are made. Sodium phosphate is the most common soluble phosphate, and hence it is the one employed for the preparation of the insoluble phosphates.

**656.** The **official orthophosphates** are:

$\text{H}_3\text{PO}_4$ , Hydrogen phosphate, or phosphoric acid; acidum phosphoricum. Colorless liquid.

$\text{K}_2\text{HPO}_4$ , Potassium phosphate; potassii phosphas. White, or colorless, crystalline. Soluble.

$\text{Na}_2\text{HPO}_4$ , Sodium phosphate. White powder. Soluble.

$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , Crystallized sodium phosphate; sodii phosphas. Colorless, crystalline. Readily soluble.

$\text{NaH}_4\text{NHPO}_4 \cdot 4\text{H}_2\text{O}$ , Sodium-ammonium-hydrogen phosphate; "microcosmic salt." Colorless, crystalline. Readily soluble.

$(\text{H}_4\text{N})_2\text{HPO}_4$ , Ammonium phosphate; ammonii phosphas. Colorless, crystalline. Readily soluble.

$\text{Ca}_3(\text{PO}_4)_2$ , Calcium phosphate; calcii phosphas; tricalcium phosphate. White, amorphous powder. Insoluble.

$\text{CaHPO}_4$ , Calcium hydrogen phosphate. White, crystalline powder. Insoluble.

$\text{CaH}_4(\text{PO}_4)_2$ , Acid calcium phosphate. Colorless. Soluble.

$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , Ferrous phosphate. Grayish-blue, amorphous. Insoluble powder.

$\text{FePO}_4 \cdot \text{H}_2\text{O}$ , Ferric phosphate. Nearly white, amorphous. Insoluble powder.

**657. Reactions of phosphates.** The metallic phosphates insoluble in water are soluble in hydrochloric acid and in nitric acid.

When heated to redness with sodium carbonate the phosphates yield sodium pyrophosphate.

At a still higher heat the pyrophosphates are converted into metaphosphates.

Soluble phosphates give a light yellow precipitate with silver nitrate solution; after having been heated to redness they give a white precipitate with that reagent, having been converted into pyrophosphates by the heat. The precipitate is soluble in nitric acid, and also in ammonia water.

Soluble phosphates give with calcium chloride a white precipitate which is readily soluble in acids, including acetic acid.

Ammonium chloride, magnesium sulphate and any soluble phosphate, when contained together in one solution, produce a white precipitate with ammonia; in dilute solutions, or when little phosphate is present, this precipitate is slowly formed.

Minute amounts of phosphates are detected with ammonium molybdate solution acidulated with nitric acid until clear; when a liquid containing a phosphate and free nitric acid, or a solution of the phosphate in dilute nitric acid, is added and the mixture warmed, a yellow precipitate or yellow coloration is produced according to the amount of phosphate present.

**658. Metaphosphates.** Metaphosphoric acid is a di-metacid,  $\text{HPO}_3$ . It is the acid first formed when  $\text{P}_2\text{O}_5$  is dissolved in water. But a water-solution of metaphosphoric acid changes gradually to orthophosphoric acid on standing, and is rapidly converted into orthoacid when boiled.

Orthophosphoric acid is converted first into pyrophosphoric and then into metaphosphoric acid by strong heat.

The colorless ice-like solid called "glacial phosphoric acid" is an impure metaphosphoric acid, containing sodium salt.

Soluble metaphosphates give a white precipitate with silver nitrate.

**659. Pyrophosphates** are the salts of pyrophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_7$ , which is derived from two molecules of  $\text{H}_3\text{PO}_4$  by the separation of three molecules of water, or may be regarded as formed from  $\text{P}_2\text{O}_5$  by combination with two molecules of water.

Orthophosphates are converted into pyrophosphates when heated to redness, by loss of the elements of water.

The most common water-soluble pyrophosphate is that of sodium.

Ferric pyrophosphate is insoluble in water, but soluble in the solution of any alkali citrate.

Sodium pyrophosphate gives a white precipitate with silver nitrate.

**660. Hypophosphites.** Hypophosphorous acid,  $\text{HPH}_2\text{O}_2$ , is a peculiarly constructed acid, for the acidic element is directly united to two hydrogen atoms. In accordance with the common method of writing the molecular formulas of acids and salts we write  $\text{HPH}_2\text{O}_2$ , or even  $\text{HH}_2\text{PO}_2$ ; but the structure is more clearly indicated by the formula  $\text{HOPH}_2\text{O}$ .

The *official hypophosphites* are:

$\text{HPH}_2\text{O}_2$ , Hypophosphorous acid; acidum hypophosphorosum. Colorless liquid.

$\text{KPH}_2\text{O}_2$ , Potassium hypophosphite; potassii hypophosphis. White, crystalline. Soluble.

$\text{NaPH}_2\text{O}_2$ , Sodium hypophosphite; sodii hypophosphis. White, crystalline. Soluble.

$\text{Ca}(\text{PH}_2\text{O}_2)_2$ , Calcium hypophosphite; calcii hypophosphis. White, crystalline. Soluble.

$\text{Fe}(\text{PH}_2\text{O}_2)_2$ , Ferrous hypophosphite. Grayish-white, amorphous powder. Insoluble.

$\text{Fe}(\text{PH}_2\text{O}_2)_3$ , Ferric hypophosphite; ferri hypophosphis. Grayish-white amorphous powder. Practically insoluble.

*Solubility.*—The hypophosphites of the alkali metals and the alkaline earth metals are *water-soluble*; those of other metals

*insoluble* in water. But ferric hypophosphite dissolves in a strong, warm solution of citrate of sodium or ammonium.

*Preparation.*—Calcium hypophosphite is *produced* by boiling phosphorus with calcium hydroxide. The other water-soluble hypophosphites are made from calcium hypophosphite by double decomposition resulting in the formation of an insoluble calcium salt (oxalate or carbonate) as a bye-product, and the insoluble hypophosphites are made from the sodium hypophosphite.

Hypophosphorous acid may be made from calcium hypophosphite and oxalic acid.

*Chemical behavior.*—The hypophosphites are reducing agents. They are easily oxidized to phosphates. When warmed or triturated with oxidizing agents they sometimes cause explosions.

## CHAPTER XXXVIII.

### CARBON.

Symbol, C. At.w., 12.

**661. Occurrence.** Carbon exists in Nature in the free state, pure and impure, as diamond, graphite and amorphous carbon in the form of soft coal, hard coal, brown coal and peat.

Combined carbon occurs throughout the vegetable and animal kingdoms in great abundance. Limestone, chalk and marble are different forms of calcium carbonate, and other metallic carbonates also exist in Nature.

Carbon is a solid, inodorous, tasteless, insoluble in all known solvents, infusible, non-volatile. It is combustible.

*Diamond* is pure carbon in the form of crystals of the regular system. It is the hardest substance known and possesses unsurpassed luster and brilliancy. It is used for cutting glass, and as a gem.

*Graphite* is also crystalline in monosymmetric forms, but not in well defined crystals. It is the so-called "plumbago" used in the composition of lubricants and in the manufacture of stove-polish, and the "black lead" of lead pencils and of graphite crucibles.

*Amorphous carbon* occurs in nature in various forms, more or less impure. Large deposits of carbon have been formed by the slow decomposition of vegetable matter under greater or less pressure.

*Peat* contains about 60 per cent of carbon; brown coal or *lignite* about 67 per cent; *bituminous* or *soft coal* about 87 per cent; and *anthracite* or *hard coal* about 94 per cent of carbon.

*Coke* is a hard, porous form of carbon formed as a residue in the manufacture of illuminating gas from bituminous coal, or manufactured specially by similar methods for use as a fuel. Coke contains more carbon than bituminous coal, but less than anthracite.

*Wood charcoal* is formed by the combustion of wood in an in-

sufficient supply of air, which leaves most of the carbon unconsumed. The method of production of charcoal is a form of "destructive distillation" with the difference that the volatile decomposition products are not collected.

*Animal charcoal* is made in the "destructive distillation," or by incomplete combustion, of animal refuse, such as bones and blood. It is called "boneblack," and a better grade of it "ivory black."

Wood charcoal is employed for fuel, and animal charcoal as a decolorizing and deodorizing agent.

*Lamp black* is a very pure carbon formed by the imperfect combustion of resinous matter and other substances rich in carbon compounds containing a high percentage of that element. Soot is also carbon.

Vegetable charcoal and animal charcoal are described in several of the pharmacopœias.

**662. Chemical properties.** At common temperatures carbon has no chemical energy. At high temperatures it unites readily with oxygen, the heat of the reaction being more than sufficient to maintain the combustion. With the aid of heat it may be used as a reducing agent.

The carbon atom in combination is a tetrad, except in CO.

The ability of carbon atoms to form chains or rings which form the skeletons of numerous organic compounds is its most striking characteristic. Its polarity-value may be  $-4$ , or  $-2$ , or  $0$ , or  $+2$ , or  $+4$ . In many organic compounds the algebraic sum of the units of positive and negative combining value of all the carbon atoms in one molecule is  $0$ . In very simple compounds a single carbon atom may be united by two of its bonds to a positive element and by the other two to a negative element, as in  $H_2CCl_2$ .

Among the compound radicals formed by carbon are  $HC$ ,  $H_2C$ ,  $H_3C$ ,  $CO$ ,  $CN$ , and many others.

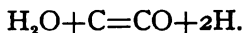
**663. Compounds.** The compounds of hydrogen and carbon are called *hydrocarbons*.

The simplest saturated hydrocarbon is the so-called "marsh-gas" or methane,  $H_4C$ . The saturated hydrocarbons are chemically indifferent. Those containing a relatively small number of carbon atoms are gases; others containing a larger proportion of carbon are liquid; while those containing a still larger proportion

of carbon are solids. Several distinct series of hydrocarbons exist among which the marsh gas series and the benzene series are especially important to the pharmacists. Coal oil is a mixture of hydrocarbons. Benzin, gasolin, petrolatum, paraffin, naphthalin, terebene and benzol are familiar examples of hydrocarbons. Most of the volatile oils are mixtures containing one or more kinds of hydrocarbons. The coal gas used for illumination and fuel is a mixture of gaseous hydrocarbons, chiefly  $H_4C$ .

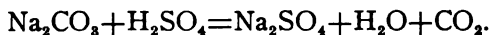
The *oxides* of carbon are the monoxide,  $CO$ , and the dioxide,  $CO_2$ .

*Carbon monoxide* is a colorless, odorless, tasteless gas, which burns with a blue flame to  $CO_2$ . It is poisonous when inhaled. Carbon monoxide is formed together with hydrogen when steam is blown through incandescent coal or coke:



This mixture of carbon monoxide and hydrogen is called *water gas*.

*Carbon dioxide*,  $CO_2$ , is present in the atmosphere because exhaled by animals, and under certain conditions by plants, produced also by the decay of animal matter, and by combustion. It can be readily prepared by decomposing carbonates with the acids:



Carbon dioxide is commonly called "carbonic acid gas." It is a colorless, slightly pungent gas of a refreshing faintly acidulous taste. At ordinary temperatures and pressure it dissolves in an equal volume of water; but *carbonic acid water*, commonly and erroneously called "soda water," is a saturated solution of carbonic acid,  $H_2CO_3$ , made by forcing carbon dioxide into ice cold water under very strong pressure—about 50 to 60 pounds to the square inch. Carbon dioxide is poisonous and even small proportions of it render the air unfit to be breathed. Effective ventilation is necessary to remove the  $CO_2$  which is injected into the air of rooms by respiration. Men and animals inhale air and exhale carbon dioxide; plants decompose the carbon dioxide appropriating the carbon and liberating the oxygen.

*Carbon disulphide*,  $\text{CS}_2$ , is an important substance. It is liquid, and largely used as a solvent.

Carbon forms several compounds with the *halogens*; but these are of little importance in pharmaceutical chemistry.

With *nitrogen* carbon forms the highly interesting compound halogen called cyanogen,  $\text{CN}$ , which combines with itself to form cyanogen gas,  $(\text{CN})_2$ . This forms hydrocyanic acid,  $\text{HCN}$ .

*Cyanogen* is a colorless gas having a very characteristic irritating odor. It is very poisonous. At  $-20^\circ \text{C}$ . it becomes liquid, and at  $-35^\circ$  congeals to an ice-like solid. When ignited it burns with a purple flame, forming carbon dioxide and free nitrogen. Cyanogen is obtained by heating mercuric cyanide.

The hydroxyl acid formed by carbon is *carbonic acid*,  $\text{H}_2\text{CO}_3$ . [Oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , is not an inorganic hydroxyl acid, but an organic carboxyl acid containing the group  $\text{COOH}$ , which characterizes all acids of the same class.]

**664. Carbonates.** Carbonic acid is a meta-acid. It exists only in water-solution, and at the ordinary temperature and pressure only a small amount of carbonic acid can be held in solution. Whenever carbonic acid is formed by decomposing a carbonate with a stronger acid, the carbonic acid,  $\text{H}_2\text{CO}_3$ , breaks up into carbon dioxide,  $\text{CO}_2$ , and water,  $\text{H}_2\text{O}$ . Carbonic acid is, therefore, a very weak acid and its salts are, as a rule, unstable. Only the alkali carbonates can be strongly heated without decomposition. All other metallic carbonates are decomposed by heat (undergo calcination).

Only carbonates of comparatively strong basic elements have a normal structure under ordinary conditions.

*Acid carbonates*, commonly called bicarbonates, are formed by potassium, sodium, lithium, ammonium, the alkaline earth metals, and magnesium, and other acid metallic carbonates exist in water-solutions. But the common carbonates of magnesium, zinc, and lead are basic in composition. Very few of the heavy metals form stable carbonates or carbonates of definite composition. When solutions of the salts of the heavy metals are mixed with solutions of the alkali carbonates, the metallic carbonates which are formed by metathesis and precipitated decompose rapidly so that carbon dioxide passes off with effervescence.

The bicarbonates are easily converted into normal carbonates by heat, carbon dioxide being disengaged:



All carbonates effervesce on the addition of the common acids, giving off  $\text{CO}_2$ .

The only water-soluble normal metallic carbonates are those of potassium and sodium. The acid carbonates of calcium and magnesium are soluble. Ammonium carbonate is also water-soluble.

Potassium carbonate and sodium carbonate are manufactured on an immense scale by processes which will be described later on in connection with the metals.

The insoluble metallic carbonates are produced by precipitation, sodium carbonate being one of the factors.

**685.** The **official carbonates** include:

$\text{K}_2\text{CO}_3$ , Potassium carbonate; anhydrous. White powder. Freely soluble.

$2\text{K}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ , probable composition of the common potassium carbonate; potassii carbonas. White powder. Freely soluble.

$\text{KHCO}_3$ , Potassium bicarbonate; potassii bicarbonas. Colorless crystals. Soluble.

$\text{Na}_2\text{CO}_3$ , Sodium carbonate; anhydrous. White powder. Freely soluble.

$\text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ , Dried sodium carbonate; sodii carbonas exsiccatus. White powder. Freely soluble.

$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , Crystallized sodium carbonate; sodii carbonas. Colorless crystals. Freely soluble.

$\text{NaHCO}_3$ , Sodium bicarbonate; sodii bicarbonas. White powder or porous masses. Soluble.

$\text{Li}_2\text{CO}_3$ , Lithium carbonate; lithii carbonas. White powder. Sparingly soluble.

$(\text{H}_4\text{N})_2\text{CO}_3$ , Normal ammonium carbonate. White. Soluble.

$\text{H}_4\text{NHCO}_3$ , Ammonium bicarbonate. White powder. Soluble.

$\text{H}_4\text{NHCO}_3 \cdot \text{H}_4\text{NH}_2\text{NCO}_2$ , The ordinary official ammonium carbonate; ammonii carbonas. Colorless, crystalline. Soluble.

$\text{CaCO}_3$ , Calcium carbonate; calcii carbonas. White powder. Insoluble.

$\text{SrCO}_3$ , Strontium carbonate; strontii carbonas. Insoluble white powder.

$\text{BaCO}_3$ , Barium carbonate; barii carbonas. Insoluble white powder.

$\text{Mg}_3(\text{OH})_2(\text{CO}_3)_4$ , Magnesium carbonate; magnesii carbonas. Insoluble, light, white powder.

$\text{Zn}_3(\text{OH})_6(\text{CO}_3)_2$ , Zinc carbonate; zinci carbonas. Insoluble white powder.

$\text{Pb}_3(\text{OH})_4(\text{CO}_3)_2$ , Lead carbonate; plumbi carbonas. Insoluble white powder.

$(\text{OBi})_2\text{CO}_3 \cdot \text{H}_2\text{O}$ , Bismuth subcarbonate; bismuthi subcarbonas. Insoluble white powder.

**666. Cyanides.** These compounds contain the negative compound halogen cyanogen, CN. The structure of the cyanides is analogous to that of the halides.

The cyanogen radical, CN, has one free carbon bond:  $-\text{C}\equiv\text{N}$ . It is frequently written Cy instead of CN.

The most important cyanides of pharmaceutical chemistry are:

HCy, Hydrocyanic acid; acidum hydrocyanicum; "prussic acid." Colorless liquid.

KCy, Potassium cyanide; potassii cyanidum. White masses. Freely soluble. Deliquescent.

AgCy, Silver cyanide; argenti cyanidum. White, amorphous, insoluble powder.

HgCy<sub>2</sub>, Mercuric cyanide; hydrargyri cyanidum. Colorless or white, crystalline. Soluble.

All cyanides are poisonous, and hydrocyanic acid is one of the most powerful of all poisons known, producing a fatal effect almost instantly when taken or inhaled in even very small quantities.

The cyanides enumerated in the foregoing table are water-soluble except the silver cyanide.

Cyanides generally form hydrocyanic acid when decomposed by hydrochloric acid, and may, therefore, be identified by the peculiar bitter-almond-like odor thus developed.

Water-soluble cyanides give a curdy precipitate of silver cyan-

ide with a solution of silver nitrate; this precipitate, like silver chloride, is insoluble in nitric acid and soluble in ammonia, but is easily decomposed by heat.

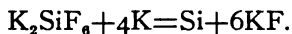
When a few drops of a solution of ferrous sulphate and ferric sulphate together is added to a solution of a cyanide, and then an excess of hydrochloric acid, a blue precipitate of ferric ferrocyanide is formed.

## CHAPTER XXXIX.

### SILICON.

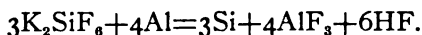
**667. Silicon**, Si., at. w., 28.4, is, next to oxygen, the most abundant of all elements. It does not occur in the free state, but a large proportion of the rock, sand and clay formations of the earth's surface consists of silica and silicates. *Silica*, or silicon dioxide,  $\text{SiO}_2$ , occurs in nature in a variety of forms called flint, agate, quartz, etc.

**668. Description.** Silicon is a solid and exists in three allotropic modifications analogous to those exhibited by carbon, with which silicon is in many respects parallel. Amorphous silicon is obtained as a brown powder when potassium silicofluoride is heated with metallic potassium:



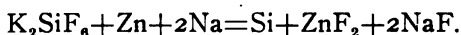
Intense heat renders this amorphous powder more dense.

A crystalline silicon is formed by the ignition of potassium silicofluoride and aluminum:



Upon treating the fused mass with hydrochloric acid and hydrofluoric acid in succession to remove the aluminum fluoride the silicon is obtained in a crystalline condition and of black color, resembling graphite.

Octohedral crystals, hard enough to cut glass, are formed when potassium silicofluoride, sodium and zinc are ignited together and the fused mass treated with hydrochloric acid and then nitric acid:



Potassium silicate is  $\text{K}_4\text{SiO}_4$  and  $\text{HCl}$  decomposes it, liberating gelatinous silicic acid,  $\text{H}_4\text{SiO}_4$ . Common silicic acid is  $\text{H}_2\text{SiO}_3$ .

**669. Uses** of silicon compounds. As silica and other silicon compounds generally are not easily decomposed or affected by other substances nor by even great changes of temperature these

compounds are utilized in the manufacture of brick, earthenware, porcelain, glass, and various other materials. Sand is silica, and clay is a more or less impure hydrated aluminum silicate; "pipe-clay," "china-clay" and "kaolin" are common names given to various grades of white clay.

Kaolin is a silicate derived from normal silicic acid,  $H_4SiO_4$ ; but the silicates of glass are derived from meta-silicic acid,  $H_2SiO_3$ .

The silicates of potassium, sodium, calcium and lead are the chief constituents of **glass**. The alkali silicates are water-soluble, but mixtures of these with calcium and lead silicates are insoluble and even resist the action of acids and alkalies to a remarkable degree.

*Hard glass*, not easily fused, consists of the silicates of potassium and calcium. The best glass of this kind is called Bohemian glass, because the sand required for its manufacture is found plentifully in Bohemia, and glass making has long been an important industry in that country. Bohemian glass is the hardest, most difficult to fuse, and resists the action of chemicals better than other kinds. Chemical apparatus is, therefore, preferably made of such glass.

*Bottle glass*, or *green glass*, consists of calcium silicate and sodium silicate, and it contains a larger proportion of the calcium salt than any other kind of glass. It resists the action of chemicals better than flint glass or crown glass, but not as well as Bohemian glass. The materials employed in the manufacture of common bottle glass are less pure than those used in making other kinds. The presence of small quantities of ferrous silicate gives bottle glass a green color. But coloring substances are often added. The Pharmacopœia orders that the solutions of the fixed alkalies be kept in "green glass" bottles, not because that glass is green, but because its composition is such as enables it to resist the action of the alkali better. Solutions of potassium or sodium hydroxide affect flint glass very decidedly, and especially the ground surfaces of the glass stoppers and necks of bottles so that the stoppers frequently become fixed or united to the necks so firmly that they can not be removed. Even bottle glass is attacked by alkalies to some extent. Hence the stoppers should be coated with petrolatum, which prevents the adhesion of

the ground surfaces because the petrolatum is not acted upon by the alkali.

*Flint glass* consists of the silicates of potassium and lead. It is comparatively readily fusible and very brilliant. But flint glass is more easily attacked by strong alkalies and acids than any other glass.

*Crown glass*, or *window glass*, is a *soft glass*, more readily fusible than any other kind. Plate glass is of the same composition. It contains chiefly sodium and calcium silicates. Soft, readily fusible glass has many uses in the laboratory for glass tubing, which is to be bent, fused, or in any way shaped and adapted for various kinds of apparatus.

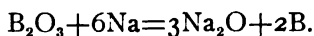
*Soluble glass*, or "water glass," is a water-solution of sodium silicate. It is used for surgical dressings, as a protective, and as an adhesive paste for labels on tin cans.

## CHAPTER XL.

### BORON.

Symbol, B. At.w., 11.

**670.** Boron occurs in nature only combined with other elements, chiefly as crude borax, called "tincal," and as impure boric acid. Thibet, Italy, and California furnish all our raw borax and boric acid. Borax is sodium tetraborate,  $\text{Na}_2\text{B}_4\text{O}_7$ , and boric acid is  $\text{H}_3\text{BO}_3$ . Boric acid, when strongly ignited, leaves boron trioxide,  $\text{B}_2\text{O}_3$ , and this, when heated with sodium, gives up its oxygen to the sodium:



Boron obtained in this way is an amorphous greenish-brown powder. This can be dissolved in fused aluminum and crystallizes from this solution on cooling, after which the aluminum is removed by solution in hydrochloric acid, leaving the yellowish octohedral crystals of boron which are nearly as hard as diamond.

**671. Borates.** Boric acid,  $\text{H}_3\text{BO}_3$ , is a normal acid. The only other normal borate employed in pharmacy is glyceryl borate,  $\text{C}_3\text{H}_5\text{BO}_3$ , commonly called "boro-glyceride" or "boroglycerin."

Boric acid, borax and glyceryl borate are all colorless water-soluble solids. They impart a green color to flame; this reaction is readily obtained by dissolving or mixing the test-sample with alcohol and burning the solution or mixture.

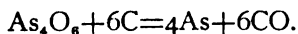
## CHAPTER XLI.

### ARSENIC.

Symbol, As. At.w. 75.

**672. Occurrence and preparation.** This element occurs in the free state but more abundantly in the form of sulphides and other compounds. The most common arsenical ores are realgar,  $\text{As}_2\text{S}_2$ ; orpiment,  $\text{As}_2\text{S}_3$ ; arsenical pyrites,  $\text{FeAsS}$ ; and "kupfer-nickel,"  $\text{NiAs}$ .

"Metallic arsenic" is produced by the reduction of its oxide,  $\text{As}_4\text{O}_6$ , by means of charcoal, a mixture of these two substances being heated together:



The free arsenic sublimes.

The so-called "cobaltum" of commerce is impure arsenic.

**673. Properties.** Arsenic is a dark steel-gray, brittle solid of metallic luster. It exists in a crystalline form as well as in an amorphous condition. The sp. w. of crystalline arsenic is 5.76; that of the amorphous variety is 4.71. At ordinary temperatures it is odorless. It volatilizes without fusion at  $450^\circ \text{C}$ ., forming brownish-yellow vapors having a strong garlicky odor.

The molecule of arsenic is tetratomic as shown by its vapor density, below  $1700^\circ$ ; but they are diatomic above that temperature.

Arsenic is chemically not a metallic element, although it is rather heavy and has metallic luster when not tarnished. It unites with hydrogen, which no true metal does, and no salts are known in which arsenic performs basic functions, while this element does perform acidic functions, forming arsenites and arsenates. Arsenic also forms sulpharsenites and sulpharsenates.

The polarity-value of arsenic is  $-3$  in arsine and other arsenides,  $+3$  in arsenites and  $+5$  in arsenates. Toward the halogens and toward oxygen and sulphur it acts with positive polarity and an atomic combining value of  $+3$  or  $+5$ .

**674. Compounds.** The compounds of arsenic are analogous in structure to those of nitrogen, phosphorus and antimony, and to some extent to those of bismuth.

Nitrogen and phosphorus lack any metallic properties; but as the atomic weights of the members of this family of elements increase, metallic properties gradually become manifest, and in bismuth very decided. The hydrogen compounds of the elements of the nitrogen group indicate the same gradation from non-metallic to metallic behavior, for ammonia (or "amine"),  $\text{H}_3\text{N}$ , is stable and alkaline; phosphine,  $\text{H}_3\text{P}$ , is less stable and only feebly, if at all, basic; arsine,  $\text{H}_3\text{As}$ , and stibine,  $\text{H}_3\text{Sb}$ , are very unstable and furnish no indication of forming any compounds similar to the ammonium compounds; and bismuth does not combine with hydrogen, although it performs basic functions but feebly.

*Hydrogen arsenide*, or arsine,  $\text{H}_3\text{As}$ , still often called "arsenuretted hydrogen," is a very poisonous gas of garlicky odor.

The *oxides* of arsenic are arsenous oxide,  $\text{As}_2\text{O}_3$ , and arsenic oxide,  $\text{As}_2\text{O}_5$ . Both are acidic anhydrides.

*Arsenous oxide* has been commonly called "white arsenic," and in the Pharmacopœia "arsenous acid." Its molecular formula has heretofore been written  $\text{As}_2\text{O}_3$ ; but its vapor density shows that it is  $\text{As}_4\text{O}_6$ .

*Chloride, bromide and iodide* of arsenic also exist. The chloride,  $\text{AsCl}_3$ , is a colorless liquid. The iodide,  $\text{AsI}_3$ , is a solid and is officinal.

The *sulphides* are the red disulphide,  $\text{As}_2\text{S}_2$ , and the yellow trisulphide,  $\text{As}_2\text{S}_3$ , both of which are solids, insoluble in water.

The most important *acids* formed by arsenic are *arsenous acid* forming *arsenites*, and *arsenic acid* forming *arsenates*.

**675. Arsenites and arsenates.** The *arsenites* are analogous in structure to the phosphites and antimonites. A solution of arsenous acid,  $\text{H}_2\text{HAsO}_3$ , and one of potassium arsenite,  $\text{K}_2\text{HAsO}_3$ , are officinal. Potassium metarsenite,  $\text{KAsO}_2$ , is contained in the arsenical solutions of some pharmacopœias.

*Arsenates* are analogous to the phosphates, and the pyroarsenates to the pyrophosphates. Sodium arsenate is officinal.

$\text{Na}_2\text{HAsO}_4$  is dried sodium arsenate. White powder. Soluble.

$\text{Na}_2\text{HAsO}_4 \cdot 2\text{H}_2\text{O}$  is effloresced sodium arsenate. White powder. Soluble.

$\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  is crystallized sodium arsenate. Colorless crystals. Readily soluble.

$\text{Na}_4\text{As}_2\text{O}_7$  is dry sodium pyroarsenate. Colorless crystals. Soluble.

**676.** Arsenical compounds have various colors, some being white or colorless, others red or yellow.

The least readily **soluble** officinal compound of arsenic is arsenous oxide or anhydride. The most freely water-soluble arsenical salt is sodium arsenate; but potassium arsenite and arsenous iodide are also water-soluble. The arsenites and arsenates of magnesium and of iron are *insoluble* in water, but soluble in dilute hydrochloric acid.

**677.** The materials employed for the **preparation** of the officinal arsenical compounds are arsenic, arsenous anhydride, and the arsenites and arsenates of the alkali metals. Metallic arsenic is employed for the preparation of the iodide, and arsenous anhydride for the preparation of "Fowler's solution" and "solution of arsenous acid." Sodium arsenate is also made from arsenous oxide or anhydride, for the arsenites may be readily oxidized to arsenates by nitric acid and other nitrates.

The insoluble arsenates and arsenites can be made from the soluble alkali arsenates and arsenites by precipitation.

**678. Officinal arsenical preparations** are presented here:

Arsenous anhydride,  $\text{As}_2\text{O}_3$ ; called acidum arsenosum, arsenous acid. White or colorless masses, or white powder. Sparingly soluble.

Arsenous iodide,  $\text{AsI}_3$ ; called arseni iodidum, iodide of arsenic. Orange-red, crystalline. Soluble.

Sodium arsenate,  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ; sodii arsenas. Colorless, crystalline. Readily soluble.

Iron arsenate; ferri arsenas. This is a ferroso-ferric compound of indefinite composition. Grayish-blue, amorphous powder. Insoluble.

Solution of arsenous acid; liquor acidi arsenosi. This contains about 1.27 Gm. of  $\text{H}_3\text{AsO}_3$ , or the quantity of arsenous acid formed by 1 Gm. of arsenous oxide,

in each 100 milliliters. But the solution probably contains also some arsenous chloride, for it is prepared by dissolving the arsenous anhydride in water containing two per cent of hydrochloric acid. Colorless.

Solution of potassium arsenite; liquor potassii arsenitis. Often called "Fowler's solution." This contains about 2 Gm. of  $K_2HAsO_3$ , which is the amount formed by 1 Gm. of  $As_4O_6$ , in each 100 milliliters. Colored reddish with santalum.

Solution of sodium arsenate; liquor sodii arsenatis. Contains 1 Gm. of dry or anhydrous  $Na_2HAsO_4$  in each 100 milliliters, being, therefore, not much more than one-half of the arsenical strength of the other solutions. Colorless.

Solution of iodide of arsenic with mercury; liquor arseni et hydrargyri iodide. This is commonly called "Donovan's Solution," and contains in each 100 milliliters 1 Gm. of arsenous iodide,  $AsI_3$ , and 1 Gm. of mercuric iodide. Pale yellow.

It will be seen that the liquid preparations of arsenic are not of uniform strength, as they were probably intended to be. Solution of arsenous acid and Fowler's solution are of equal arsenical strength; but the arsenical strength of solution of sodium arsenate *expressed in terms of arsenous oxide* is 0.53 per cent, or 0.53 as strong as the other two. Donovan's Solution has *less than one-fourth* the arsenical strength of Fowler's solution.

Arsenical preparations are "alterative" in their effects. They are all very poisonous.

**679. Modes of administration.** *Arsenous oxide* ("arsenous acid") and iron arsenate are prescribed in pill form.

*Arsenous iodide* is used only for the preparation of Donovan's solution, and *sodium arsenate* only in the form of its official solution.

The liquid arsenical preparations ought not to be prescribed undiluted, because the doses are so small that they can not be accurately apportioned by persons unpracticed in dropping and counting drops of approximately definite size. Distilled water

is the best diluent and should be prescribed with the arsenical solutions in such proportion that the dose will be one medicinal teaspoonful, or 5 milliliters, and this volume should be measured out *not* with a spoon, but in a graduated glass measure.

Arsenical solutions should be prescribed alone, i. e., not mixed with other medicinal substances, because they are incompatible with many remedies, both organic and inorganic.

**680.** The *symptoms of poisoning* from arsenic are: Constriction and heat of the fauces, burning pain in the abdomen, nausea, vomiting, thirst, bloody evacuations, strangury, spasms, dyspnoea, and collapse.

The *antidotal measures* are: prompt evacuation of the stomach by means of powerful, rapidly acting emetics, such as zinc sulphate, alum, copper sulphate or mustard, with plenty of warm water, or by means of the stomach pump. Afterwards chemical antidotes should be administered, namely such substances as produce insoluble compounds with arsenic. The best chemical antidotes are light magnesia mixed with water; the "antidote for arsenic" of the Pharmacopœia, bearing the antiquated title "hydrated oxide of iron with magnesia," is also suitable; freshly precipitated ferric hydroxide; and solution of ferric acetate. Threatened collapse may be averted by the application of hot water to the limbs and back of the patient by means of rubber bags or bottles, or by the use of hot bricks or flat-irons wrapped in cloths. The cautious administration of alcoholic stimulants may also be used, and opiate enemas.

**681. Reactions.** Arsenic and its compounds may be *identified* by various methods. The principal *tests* are the following:

1. As the metal is volatile, and as its vapor has a disagreeable characteristic garlic odor, and condenses to form shining rhombohedral crystals (or an amorphous brown-black film if the quantity is small), compounds of arsenic may be identified by the aid of these signs, or one of them, whenever it is practicable to effect the dissociation of the compound and reduce it to metallic arsenic.

Thus, when heated with dried sodium carbonate upon charcoal in the inner blow-pipe flame, arsenical compounds evolve the odor of garlic.

A small quantity of the arsenous anhydride may be put in the end of a glass tube drawn out to a narrow point and sealed at that end, a little splinter of charcoal, previously thoroughly

heated, placed in front of it, the tube then held in the flame of a Bunsen burner and heated only at the point where the charcoal rests, until glowing, after which the end of the tube where the suspected substance lies, is also heated. The arsenic compound, if any be present, is vaporized, the gas passing over the glowing charcoal is reduced, and the metallic arsenic condenses further up in the tube, forming a shining mirror.

When a small portion of well dried arsenous anhydride is put in the bulb of an arsenic reduction tube, and over it a thoroughly dried mixture of potassium cyanide and sodium carbonate, the bulb being then heated, metallic arsenic is sublimed and may be recognized by the mirror it forms, by the garlic odor produced when that mirror is vaporized, and by the crystalline sublimate of arsenous anhydride obtained when the metal is again heated in the tube and thus oxidized by combustion in the air which it contains.

2. Arsenous anhydride, heated in a glass tube of small diameter, sublimes and condenses in the cooler upper part of the tube, forming a deposit of octohedral crystals.

3. If a little of any arsenous compound be boiled with water in a test-tube, the liquid acidified with hydrochloric acid, and hydrogen sulphide then introduced, a yellow precipitate of arsenic trisulphide will be formed.

An arsenic compound similarly treated produces a yellow precipitate of trisulphide together with free sulphur.

4. If a soluble arsenous compound be dissolved in a little water, a drop of test-solution of silver nitrate added, and then a drop or two of ammonia water, a yellow precipitate of silver arsenite will be formed.

When copper sulphate test-solution, instead of silver nitrate, is used, a yellowish-green precipitate of copper arsenite is formed.

If the substance tested be an arsenic instead of an arsenous compound, the silver nitrate will produce a red-brown precipitate of silver arsenate, and the copper sulphate a bluish-green precipitate of copper arsenate.

These precipitates, both arsenous and arsenic, are soluble in dilute nitric acid.

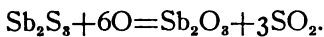
## CHAPTER XLII.

### ANTIMONY.

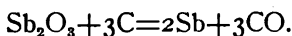
Symbol, Sb. At.w., 120.

**682. Occurrence and production.** Antimony occurs in nature to a small extent uncombined; to a much greater extent in the form of antimonous sulphide called *stibite* or *antimonite*. When this "antimony ore" is fused the accompanying, less readily fusible, mineral impurities are easily eliminated, as they are heavier, so that the melted antimony sulphide can be poured off. The product thus obtained is the "black sulphide of antimony" of commerce, which usually contains some arsenic.

Metallic antimony is produced by reduction of the "roasted" sulphide. When the black sulphide of antimony, coarsely powdered, is strongly heated, or "roasted," in free contact with the air, it is decomposed, and antimonous oxide is formed.



The oxide is then heated with charcoal, which readily reduces it to antimony:



**683. Description and uses.** Antimony is bluish-white, brittle, crystalline, and of a decidedly metallic lustre. It fuses at  $425^\circ$  to  $450^\circ$  C., and is vaporized at white heat. The vapor at about  $1640^\circ$  has a density of about 350, which would indicate triatomic molecules; but it seems probable that this vapor consists in part of tetratomic and in part of diatomic molecules.

The sp. w. of the metal is about 6.8.

The metal is employed as an ingredient in several alloys, of which the so-called "type-metal" is the most important. It is made by fusing together one part of antimony and four parts of lead. But the alloys used in type foundries and by electrotype makers sometimes contain also copper, bismuth, tin, or aluminum.

**684. Chemical properties.** Notwithstanding its decidedly

metallic appearance and its considerable density, antimony does not possess the chemical characteristics of metals, for it combines with hydrogen, forming stibine, or hydrogen antimonide,  $H_3Sb$ , which is a colorless, odorless gas, and antimony can not perform the basic function in the formation of salts. One salt, the sulphate of antimony, has been prepared, but it is described as extremely unstable and of doubtful composition or identity.

The polarity-value of negative antimony is  $-3$ ; that of positive antimony  $+3$  or  $+5$ .

**685. Compounds.** The *hydrogen* compound, already mentioned, corresponds to arsine.

The *oxides* are antimonous oxide,  $Sb_2O_3$ , and antimonic oxide,  $Sb_2O_5$ . Both are solids; the former white, the other pale yellow.

*Antimonous sulphide*,  $Sb_2S_3$ , is black when crystallized, as in the ordinary fused antimony sulphide of commerce; but the precipitated amorphous antimonous sulphide is yellowish-red. The precipitated antimonic sulphide,  $Sb_2S_5$ , is orange-red.

*Trichloride* of antimony,  $SbCl_3$ , is a soft, butter-like, volatile solid, called "butter of antimony." It is soluble in a very small amount of water, but decomposed by a larger quantity except in the presence of a considerable proportion of hydrochloric acid. The *pentachloride*, or antimonic chloride, is a volatile liquid.

Antimonites, antimonates, sulphantimonites, and sulphantimonates also exist.

**686.** Antimony compounds are white or colorless, red, yellow, brown, or black.

The only water-soluble officinal antimony compound is the antimonyl potassium tartrate. This compound is soluble in about 17 parts of water and has a sweetish, afterwards metallic, disagreeable taste.

The *material* employed for the preparation of antimony compounds is primarily the black sulphide of antimony, which may be dissolved in very strong hydrochloric acid or in solutions of the alkalis, the solutions thus obtained being then used to produce the insoluble oxychloride, oxide, and precipitated sulphide.

**687.** The **officinal antimony compounds** are:

$Sb_2S_3$ , Black antimonous sulphide; antimoni sulphidum. This is the commercial crystalline sulphide. Dark steel-gray, nearly black. Insoluble.

$\text{Sb}_2\text{S}_3$ , Purified elutriated antimonous sulphide; *antimoni sulphidum purificatum*. Antimonous sulphide in impalpable powder, freed from arsenic. Black. Insoluble.

$\text{Sb}_2\text{S}_3$ , Precipitated antimonous sulphide, or "sulphurated antimony;" *antimonum sulphuratum* of the U. S. P. A precipitated antimonous sulphide containing some oxide. Yellowish-red, insoluble amorphous powder.

Antimonic sulphide, called sulphurated antimony, or *antimonum sulphuratum*, in the British Pharmacopœia. Made by precipitation. Yellowish-red, insoluble, amorphous powder.

"Kermes mineral," or "oxysulphuret of antimony;" a precipitated antimonous sulphide containing an appreciable quantity of oxide. Now rarely employed. Soft, chocolate-brown, amorphous, insoluble powder.

Antimony oxychloride,  $\text{O}_5\text{Sb}_4\text{Cl}_2$ ; *antimoni oxychloridum*, or Algaroth's powder. White, amorphous, insoluble powder.

Antimonous oxide; *antimoni oxidum*. White, amorphous powder; or a glassy, nearly colorless, fused mass. Insoluble.

Antimonyl-potassium tartrate; *antimoni et potassii tartras*, or tartrate of antimony and potassium, or tartar emetic, having the composition  $2\text{OSbKC}_4\text{H}_4\text{O}_6$ .  $\text{H}_2\text{O}$ . White, crystalline. Soluble.

Solution of antimony trichloride; *liquor antimoni chloridi*, or solution of chloride of antimony of the British Pharmacopœia. The solution contains a considerable amount of free hydrochloric acid to prevent the formation of the insoluble oxychloride. Nearly colorless; or somewhat reddish.

The antimonial preparations are *used* as sedative diaphoretics and arterial sedatives. "Tartrate of antimony and potassium" is, in doses of fifty or more milligrams, a powerful emetic, and in minute doses a diaphoretic.

Antimonials are much less poisonous than arsenicals, probably because they are insoluble or readily form insoluble compounds.

**688.** The *symptoms of poisoning* are in many respects similar to those produced by arsenic. They include pain in the stomach, vomiting, retching, salivation, cramps, colic, frequent watery stools, dryness of the throat, cold, clammy skin, feeble pulse, slow respiration. To counteract the poisonous effects of antimony let the patient drink large quantities of tepid water to aid in washing out the contents of the stomach; then administer vegetable astringents, such as very strong green tea, infusion of nutgall or oak bark, or a solution of tannin. The depression caused by the antimony may be diminished by the use of strong coffee, alcoholic stimulants, or opium.

**689. Reactions.** Antimony compounds may be *identified* as follows:

When an antimony compound is mixed with sodium carbonate and the mixture heated upon charcoal in the inner blow-pipe flame (the "reduction flame"), the metal separates in the form of globules, while at the same time a thin, white coating of antimony oxide is deposited upon the charcoal around the metal.

Metallic zinc precipitates the antimony from acid or neutral solutions of antimony compounds, the precipitated metal assuming the form of a black powder, which is insoluble in hydrochloric acid.

Acid solutions of antimony compounds give a yellowish-red precipitate with hydrogen sulphide, this precipitate being soluble in  $H_4NSH$ , but scarcely at all in ammonia.

Alkaline solutions of sulphur salts of acidic antimony give yellowish-red precipitates with sulphuric acid.

## CHAPTER XLIII.

### TIN.

Symbol, Sn. At.w., 119.

**690. Occurrence and production.** Tin ore or tin-stone, or cassiterite, is stannic oxide,  $\text{SnO}_2$ . This is found in Cornwall, in the island of Banca, and in certain localities in Australia and America. The oxide is reduced to the metallic condition by smelting with coal.

**691. Description.** Tin possesses in a high degree the physical properties of a metal. It is silver white, of decided lustre, soft, malleable, crystalline, and fuses at  $228^\circ \text{C}$ . Its sp. w. is 7.3.

Chemically considered, tin does not act like a metal. It does not form salts in which the tin performs the basic function. A "sulphate of tin" has been mentioned, which is easily decomposed by water; but no other evidence of basic properties exists. On the other hand, tin forms salts in which it exercises acidic functions. The compounds of tin present many points of resemblance to those of carbon. Its ruling valence is that of a tetrad.

Tin is not easily oxidized, nor is it attacked by organic substances which affect iron, copper, lead, zinc, antimony, etc.

**692. Uses.** Tin is extensively employed for household utensils, for canning fruits, vegetables and other provisions, and in the construction of laboratory apparatus. Its employment for these purposes arises from the fact that it is not oxidized, nor attacked by organic acids.

Tin-plate, or, rather, tinned iron plate, is the material out of which "*tin-ware*" is made.

Copper kettles, stills, pans and other vessels are also "*tinned*" because many organic substances attack untinned copper and form poisonous copper compounds.

"*Block-tin*," or pure tin, is a suitable material for evaporating dishes, "condensing worms," measuring vessels, and other laboratory apparatus for certain pharmaceutical operations.

*Tin foil*, made of *pure* tin, is often used to enfold substances

liable to be injured by contact with air or moisture. It is also employed for certain reactions in chemical analysis. But tin foil often contains lead and is then unfit for these uses.

*Solder* is a mixture of equal parts of tin and lead, fused together.

*Pewter* is composed of three parts of tin and one of lead.

Mirrors are silvered with *tin amalgam*.

**693. Compounds.** The following examples of tin compounds show their general structure:

$\text{SnO}$ , Stannous oxide; white, insoluble.

$\text{SnCl}_2$ , Stannous chloride; white, decomposed by water.

$\text{SnS}$ , Stannous sulphide; black, insoluble.

$\text{SnO}_2$ , Stannic oxide; white, insoluble.

$\text{SnCl}_4$ , Stannic chloride; colorless liquid.

$\text{SnS}_2$ , Stannic sulphide; yellow, insoluble.

"Tin salt" is a tin chloride,  $\text{SnCl}_2$ , produced by dissolving tin in hydrochloric acid with the aid of gentle heat. On evaporation of the solution the salt is obtained in crystals containing two molecules of water,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . It is soluble in a mixture of hydrochloric acid and water, and also in a very small amount of water alone, but is decomposed when brought in contact with a large proportion of water. Tin salt is used as a mordant in dyeing and calico printing.

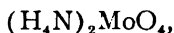
Being a "reducing agent," the  $\text{SnCl}_2$ , in solution, precipitates calomel from a solution of mercuric chloride, and gives a blue precipitate with a mixture of ferric chloride and potassium-ferricyanide in water-solution.

**694. Reactions.** Tin is precipitated from solutions of its salts by either iron or zinc. With  $\text{KOH}$  these solutions give a white precipitate soluble in an excess of the reagent. Alkali carbonates also precipitate white hydroxides. Stannous salts give a blackish-brown precipitate with  $\text{H}_2\text{S}$ ; stannic salts give a yellow precipitate with the same reagent; these precipitates are soluble in yellow solution of ammonium hydrosulphide (solution of  $\text{H}_4\text{NSH}$ , which has become yellow from polysulphides of ammonium formed by exposure to the air), but the dark-brown stannous sulphide is insoluble in pure  $\text{H}_4\text{NSH}$ , which dissolves the yellow stannic sulphide.

## CHAPTER XLIV.

### MOLYBDENUM, TUNGSTEN AND URANIUM.

**695. Molybdenum**, Mo, at. w., 96, is a hard, silver-white metal of the sp. w., 8.6. It is a comparatively rare element. Its most important compound is the trioxide,  $\text{MoO}_3$ , commonly called "molybdic acid," which is analogous to chromic anhydride, being an acidic oxide which forms salts corresponding in structure to the chromates and sulphates. Ammonium molybdate,



is an important reagent for the detection and determination of phosphoric acid and other phosphates.

Molybdenum does not perform basic functions, but molybdic acid,  $\text{H}_2\text{MoO}_4$ , forms a number of salts with the stronger bases. Polymolybdic acids, which are apparently compounds of molybdic acid with water in various proportions, and of which several are known, form rather complex salts.

Molybdenyl Sulphate,  $\text{O}_2\text{MoSO}_4$ , generally called "sulpho-molybdic acid," is used as a color reagent for the identification of certain alkaloids.

**696. Tungsten**, W (Wolframium), at. w., 184, is a very hard metal, forming lustrous steel-gray plates or a black powder. Its sp. w. is 19.13.

Its compounds are as varied and complex as those of molybdenum.

The trioxide is commonly called "tungstic acid." Tungstic acid,  $\text{H}_2\text{WO}_4$ , is known. A sodium polytungstate is used as a reagent. It is called sodium metatungstate and has the composition  $\text{Na}_2\text{W}_4\text{O}_{13} \cdot 10\text{H}_2\text{O}$ .

**697. Uranium**, U, at. w., 239.5, is a rare metal of the color of nickel. Its sp. w. is 18.4. In uranous compounds the element is a tetrad; in uranic compounds a hexad. Diuranic acid,  $\text{H}_2\text{U}_2\text{O}_7$ , corresponds to dichromic acid.

A few salts are known in which quadrivalent uranium seems to perform basic functions, as, for example,  $\text{U}(\text{SO}_4)_2$ . But *uranyl*,  $\text{UO}_2$ , which is a bivalent compound radical, forms several salts, among which are the nitrate,  $\text{O}_2\text{U}(\text{NO}_3)_2$ , and the sulphate,  $\text{O}_2\text{USO}_4$ . The nitrate is used as a reagent in the determination of phosphates.

## CHAPTER XLV.

### BISMUTH.

Symbol, Bi. At.w., 208.

**698. Occurrence and properties.** Bismuth occurs in nature uncombined but usually contaminated with arsenic, which must be removed in the manufacture of the bismuth compounds.

It is a reddish-white, brittle metal of high lustre and well developed crystalline structure. It is neither malleable nor ductile. Its sp. w. is 9.74. It melts at about  $270^{\circ}\text{C.}$ , and when the fused metal congeals it expands and is therefore used as an ingredient in certain kinds of type metal. It vaporizes at white heat.

Nitric acid dissolves bismuth, very readily forming bismuth nitrate,  $\text{Bi}(\text{NO}_3)_3$ , which is soluble in a mixture of nitric acid and water in certain proportions, but decomposed when more water is added.

Bismuth performs basic functions, but is a feeble base. It does not form any acid. Its ruling valence is that of a triad.

It does not combine with hydrogen.

**699. Compounds.** Bismuth forms several *oxides*, of which  $\text{Bi}_2\text{O}_3$  is the most important. The hydroxide is  $\text{Bi}(\text{OH})_3$ .

Halides of trivalent bismuth and a sulphide are also well known. Also *bismuthyl compounds*, as  $\text{OBiCl}$ ,  $\text{OBiI}$ ,  $\text{OBiNO}_3$ , etc.

Bismuth compounds are white or colorless, black, red or brown. They are tasteless, because insoluble, for the only water-soluble bismuth preparation known to pharmacy is the so-called ammonio-citrate of bismuth, or citrate of bismuth and ammonium.

Normal bismuth nitrate is decomposed by water, but is soluble in dilute nitric acid, in glycerin, and in glacial acetic acid. Such solutions can be used in making certain of the insoluble salts of bismuth by metathesis.

All bismuth preparations employed in pharmacy are made primarily from bismuth nitrate obtained by dissolving the metal in dilute nitric acid.

**700. The official bismuth compounds include:**

$\text{Bi}(\text{NO}_3)_3$ , Normal bismuth nitrate; bismuthi trinitras. Colorless crystals. Decomposed by water.

$\text{OBiNO}_3$ , Bismuthyl nitrate, or subnitrate of bismuth; bismuthi subnitrates. White, insoluble powder.

$(\text{OBi})_2\text{CO}_3 \cdot \text{H}_2\text{O}$ , Bismuthyl carbonate, or subcarbonate of bismuth; bismuthi subcarbonas. White, insoluble powder.

$\text{BiC}_6\text{H}_5\text{O}_7$ , Bismuth citrate; bismuthi citras. White, insoluble powder.

$\text{Bi}_2\text{O}_3$ , Bismuth oxide; bismuthi oxidum. White, insoluble powder.

$\text{OBiCl}$ , Bismuthyl chloride, or oxychloride of bismuth; bismuthi oxychloridum. White, insoluble powder.

$\text{Bi}(\text{C}_7\text{H}_5\text{O}_3)_3$ , Bismuth salicylate; bismuthi salicylas. White, insoluble powder.

$\text{Bi}(\text{C}_8\text{H}_5\text{O}_3)_3$ , Bismuth lactate; bismuthi lactas. White; insoluble.

$\text{Bi}(\text{C}_{18}\text{H}_{33}\text{O}_2)_3$ , Bismuth oleate; bismuthi oleatum. White; insoluble.

“Subgallate of Bismuth,” and “tannate of bismuth,” both of indefinite composition, are also employed in medical practice.

Normal bismuth nitrate is altogether unsuitable for medicinal uses, because it is decomposed by moisture and then liberates nitric acid.

**701. Uses.** Subnitrate and subcarbonate of bismuth are very much employed; they are usually prescribed in powders, and much less frequently in pills and tablets. The citrate is little used.

The only bismuth compound available for use in the liquid form is the ammonio-citrate of bismuth, which is soluble in water and can thus be incorporated in liquid preparations. But it is probably precipitated from any solution immediately upon being taken into the stomach.

Bismuth preparations, notably the subnitrate and subcarbonate, as found in commerce, very frequently contain arsenic, and sometimes so much that each medicinal dose of the bismuth preparation carries with it a quantity of arsenic sufficient to exert its medicinal effects when used long enough. They are quite unfit for medicinal use unless entirely free from arsenic.

**702. Reactions.** Bismuth compounds when heated on charcoal in the blow-pipe flame leave a button of metallic bismuth and a film of  $\text{Bi}_2\text{O}_3$  on the charcoal. The  $\text{Bi}_2\text{O}_3$  is reddish-yellow while hot, but becomes pale yellow on cooling. The metallic button is soluble in nitric acid, and this solution becomes turbid on the addition of enough water.

## CHAPTER XLVI.

### THE PLATINUM METALS.

**703. Platinum**, Pt, at. w., 195, occurs in nature only in the free state. It is a grayish-white lustrous metal, hard and tough, fusible only at a strong, white heat, not attacked by any acid, but soluble in "aqua regia" or nitrohydrochloric acid. The sp. w. of platinum is 21.46.

**Iridium** closely resembles platinum, but is even harder, more difficult to fuse, and heavier, having the sp. w. 22.42.

**704.** An admixture of iridium to platinum renders it harder, more resistant to the roughest treatment, and less liable to be attacked by any chemicals. Such an alloy is used for making dishes, platinum foil and wire, spatulas, weights, and other articles.

The platinum of which crucibles and dishes are made contains about 2 per cent of iridium. The "irido-platinum" employed in making the prototype standards of measures of length and mass, as of the meter and the kilogram, consists of nine-tenths of platinum and one-tenth of iridium.

But metals and easily reducible metallic compounds should not be strongly heated in platinum crucibles, because platinum forms alloys with other metals. Neither should caustic alkalies, KOH and NaOH, be fused in platinum vessels, for the metal is attacked by the alkalies. Platinum is also attacked by potassium cyanide, nitrates, mixtures which evolve free chlorine, and certain metallic sulphides, as, for instance, those of potassium and barium. Silicon and phosphorus also attack or injure platinum vessels, rendering the metal brittle. A sooty or luminous gas flame, or contact with incandescent carbon, as charcoal, causes the formation of a little platinum carbide; this is also injurious to the metal.

Platinum vessels which have been subjected to a high temperature must each time be well cleaned and rendered perfectly bright by rubbing them with a little *very fine* sand. When much attacked or soiled, platinum vessels may be cleaned by heating them in fused potassium acid sulphate,  $\text{KHSO}_4$ .

**705.** Some of the alloys of platinum dissolve in the stronger acids.

Soluble double salts of platinum are comparatively stable; its other compounds are unstable.

Platinic chloride,  $\text{PtCl}_4$ , is used as a reagent. It is a brown-red salt, soluble in water and in alcohol. It forms very sparingly water-soluble compounds with potassium and ammonium, which are insoluble in alcohol. Their formulas are  $\text{K}_2\text{PtCl}_6$  and  $(\text{H}_4\text{N})_2\text{PtCl}_6$ . But sodium-platinum-chloride is readily water-soluble.

## CHAPTER XLVII.

### GOLD.

Symbol, Au, At.w. 197.

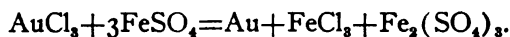
**706. Occurrence and production.** Gold occurs naturally almost exclusively in the uncombined state, in dust or nuggets, mixed with sand, gravel, and alluvial deposits, or imbedded in quartz and other minerals.

It is separated from the gold bearing gravel, dirt and quartz by *washing* away these lighter substances with slowly running water, which leaves the heavy gold.

The principal chemical processes by which gold is separated are the amalgamation process, the chlorine process and the cyanide process.

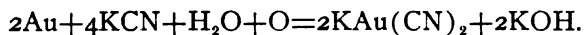
The *amalgamation process* consists in passing the ground ore, mixed with water, over copper plates coated with mercury. The gold adheres to the plates, forming an amalgam, which is collected and subjected to distillation; the mercury distills over and the gold remains.

The *chlorine process* consists in roasting the ore to remove sulphur, then mixing the roasted ore with water and exposing it to the action of chlorine in tanks for about twenty-four hours or longer. The gold is dissolved in the form of trichloride,  $\text{AuCl}_3$ . The solution is run off and ferrous sulphate is added to it, which reduces the chloride to metal:

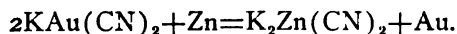


Bromine is employed in the same manner as chlorine.

The *cyanide process* is employed chiefly to extract the gold from refuse ore and the residues left by the other processes. These tailings or any low grade gold ore, ground to powder, when treated with a 5 per cent solution of potassium cyanide, give up the gold:



The solution is then treated with zinc shavings:



**707. Description.** Gold is a soft, yellow metal, capable of high polish, extremely malleable and ductile. Its sp. w. is 19.3. It melts at about 1037° C.

Acids do not affect pure gold, but it combines directly with chlorine and bromine and is soluble in "aqua regia." Alloys of gold with silver or copper, if not containing too large a proportion of gold, are easily attacked by nitric acid, which dissolves the silver or copper, leaving the pure gold, and this fact is utilized in *refining*.

*Coin gold*, the alloy of which the gold coin of America is made, consists of nine-tenths gold and one-tenth copper. An "eagle," or ten dollar gold coin, weighs 258 grains, and the "tolerance of the mint" permitted in the weight of each such coin is  $\frac{1}{2}$  grain, but the actual weight of a new "eagle" very rarely varies from the exact standard.

*Jeweler's gold* is alloyed sometimes with silver and sometimes with copper. Its "fineness" is expressed in twenty-fourths called "carats." Thus a 14 carat gold is an alloy composed of 14-24 of gold and 10-24 of the other metal.

Gold coin and old gold scraps may be used for the preparation of gold trichloride,  $\text{AuCl}_3$ , which, mixed with  $\text{NaCl}$  is the only official gold compound used for medicinal purposes. But the alloy contained in the coin or scrap gold must, of course, be removed before the salt can be made.

*Gold leaf* is used for various purposes. Thick gold leaf is used for filling tooth cavities. Thin gold leaf is used for gilding, and occasionally for coating pills.

**708.** Gold chloride and bromide are described in Vol. II. Both are water-soluble, yellow, crystalline.

## CHAPTER XLVIII.

### SILVER.

Symbol, Ag, At.w. 108.

**709. Occurrence and production.** Silver occurs in nature in the uncombined state, but more freely in the form of sulphide, associated with sulphides of lead, copper, arsenic and antimony.

It is *produced* from the ores by various processes, according to their nature. Roasting and amalgamation are both practiced. When silver ores are roasted with salt, silver chloride is formed, and the chloride is then agitated with iron and mercury, when the iron reduces the silver chloride to metallic silver, which forms an amalgam with the mercury. This amalgam is liquid. It is freed from a portion of the mercury by means of canvas filter bags through which the mercury passes, leaving a thicker, pasty amalgam richer in silver. This is then subjected to distillation, by which all of the mercury is separated, leaving metallic silver, which is fused and cast into bars or ingots.

When silver-bearing lead sulphide is roasted, and the lead oxidized to litharge in a cupellation furnace, the silver remains in a metallic state.

**710. Description.** Silver is a white metal capable of very high polish. It is soft, but harder than gold. It is malleable and ductile. Not tarnished in dry air, but traces of sulphides in the atmosphere tarnish it quickly. This metal has the sp. w. 10.6 and melts at about 916° C.

Silver is the best conductor of heat and electricity known.

*Pure silver* is called "sterling silver." *Coin silver* usually contains 10 per cent of copper; but in some countries the proportion of alloys is less or greater.

The fineness of silver used in silverware is expressed in carats in the same manner as in the case of gold.

*Silver dishes*, crucibles, spoons and spatulas are very useful in the laboratory and ought to be commonly employed now since silver has become so low-priced.

*Silver foil* is used to some extent at the dispensing table to coat

pills. But pills containing sulphides and other sulphur compounds which blacken the silver by forming silver sulphide should not be "silvered."

Tarnished silver is easily cleaned with ammonia, in which many silver compounds are soluble.

**711. Chemical properties.** Silver is a monad, and a comparatively strong base when forming salts with the stronger acids. But silver oxide is an unstable compound.

The metal is not attacked by hydrochloric acid nor by dilute sulphuric acid, and scarcely at all affected by alkalies. The alkalies and silver nitrate are necessarily fused in silver dishes. Nitric acid and hot, concentrated sulphuric acid dissolve the metal. When silver is dissolved in strong nitric acid the acid consumed for the oxidation yields both  $\text{NO}_2$  and  $\text{NO}$ ; but when the acid is dilute no  $\text{NO}_2$  but only  $\text{NO}$  is formed.

**712. Compounds.** Silver salts resemble those of lead rather than the salts of any other metal. The nitrates and acetates of lead and of silver are their only water-soluble compounds.

A number of silver compounds which are insoluble in water are soluble in ammonia solution; in this respect the compounds of silver resemble those of copper.

The following examples illustrate the structure of silver compounds:

$\text{Ag}_2\text{O}$ , Silver oxide; argenti, oxidum. Dark brown, insoluble, amorphous powder.

$\text{Ag}_2\text{S}$ , Silver sulphide; argenti sulphidum. Black, insoluble powder.

$\text{AgCl}$ , Silver chloride; argenti chloridum. White, amorphous, insoluble powder.

$\text{AgBr}$ , Silver bromide; argenti bromidum. Nearly white, amorphous, insoluble powder.

$\text{AgI}$ , Silver iodide; argenti iodidum. Pale yellow, amorphous, insoluble powder.

$\text{AgCN}$ , Silver cyanide; argenti cyanidum. White, amorphous, insoluble powder.

$\text{AgNO}_3$ , Silver nitrate; argenti nitras. Colorless crystals. Soluble.

$\text{Ag}_2\text{SO}_4$ , Silver sulphate; argenti sulphas. White, crystalline, very sparingly soluble.

$\text{AgC}_2\text{H}_3\text{O}_2$ , Silver acetate; argenti acetas. White, crystalline. Soluble.

**713.** The **official silver compounds** are the nitrate oxide, iodide, and cyanide.

The nitrate and the iodide are occasionally prescribed in pill form; they may be massed with kaolin and tragacanth. The nitrate is frequently employed in solution for external use. The oxide is extremely unreliable and ought to be discarded since more suitable oxidizing agents are available for internal use. The cyanide is used solely for the extemporaneous preparation of hydrocyanic acid by double decomposition with hydrochloric acid.

The nitrate of silver molded into pencils or cylindrical sticks is employed for external application as a "caustic," either alone or diluted with potassium nitrate.

**714. Reactions.** Solutions of silver salts give a brown precipitate of silver oxide on addition of potassium hydroxide; hydrogen sulphide precipitates black silver sulphide; hydrochloric acid produces a white precipitate soluble in ammonia water. Metallic silver is precipitated from solutions of silver salts by zinc, iron, copper or mercury, and slowly by ferrous sulphate.

## CHAPTER XLIX.

### MERCURY.

Symbol, Hg, At.w. 200.

**715. Occurrence and production.** Mercury occurs in nature in the form of crystallized mercuric sulphide called *cinnabar*. This mercury ore is roasted to eliminate the sulphur by oxidation to  $\text{SO}_2$ . The liberated metal is distilled. Or the sulphide is heated with lime in retorts to remove the sulphur.

**716. Description.** Mercury is the only metal which is liquid at common temperatures. Being silver-white, lustrous and mobile, it is called "quicksilver." Its sp.w. is 13.6, and it boils at about  $360^\circ \text{C}$ . It freezes at about  $-40^\circ \text{C}$ .

Commercial mercury is generally found contaminated with zinc, lead, and other impurities. Hence it requires purification before it can be used for the production of pharmaceutical preparations.

**717. Chemical properties.** The mercury molecule is monatomic. The metal does not readily enter into combination with oxygen at the common temperature, and it does not exhibit great chemical energy. Its compounds are generally unstable. Many are decomposed by light.

**718.** There are two series of mercury compounds: 1, The mercurous compounds, formed by univalent mercury; and 2, the mercuric compounds, formed by bivalent mercury.

The compounds of mercury are of various colors: white, colorless, scarlet, crimson, yellow, orange red, brown, and black. Several mercury compounds exist in two differently colored forms. Thus mercuric oxide may be red or yellow; mercuric iodide may be red or yellow; mercuric sulphide may be red or black.

The mercuric chloride and the nitrates of mercury have an extremely disagreeable acrid metallic taste.

The mercuric and mercurous chlorides, and mercuric iodide and sulphide, are volatile and can, therefore, be sublimed without decomposition.

Mercurous compounds may be changed into mercuric compounds by contact with oxidizing agents, or may be split up into mercuric compounds and metallic mercury under the influence of light or in contact with certain substances, as for instance with vegetable extracts.

Mercuric compounds may be reduced to mercurous compounds by trituration with more mercury; they may undergo dissociation under the influence of light or of heat.

The mercurous and mercuric nitrates are decomposed by much water and can be had in solution only in the presence of a large proportion of free nitric acid.

Mercuric sulphate is also decomposed by water, and a solution of that salt can not be made.

When mercury salts of normal composition are decomposed by water they split up into so-called "basic salts" and acid.

The only *water-soluble* mercury compounds are mercuric chloride, mercuric cyanide, and mercuric bromide.

**719.** The *materials* available for the *production* of mercury compounds are metallic mercury, mercuric chloride, mercuric oxide, and solutions of the normal nitrates of mercury in water strongly acidulated with nitric acid. Mercurous and mercuric sulphate are employed in the preparation of sublimed calomel and corrosive sublimate.

Metallic mercury dissolves readily in nitric acid and a mercurous or mercuric salt may be obtained according to the proportions employed, the strength of the acid, and the temperature.

When the metal is heated with strong sulphuric acid (with or without nitric acid added for oxidation) mercuric sulphate is formed which may be converted into mercurous salt by trituration with as much more mercury.

Mercuric oxide is formed when nitrate of mercury is decomposed by heat. Mercuric oxide is employed in preparing mercuric oleate, solution of mercuric nitrate and several other mercuric compounds.

Whenever a mercurous compound is to be made by precipitation an acid solution of mercurous nitrate must be used.

An acid solution of mercuric nitrate *can* be used for the preparation of some insoluble mercuric compounds; but not as advantageously as the mercuric chloride because the free nitric acid present is liable to cause loss or interference.

The best material for making insoluble mercuric compounds by metathesis is mercuric chloride.

**720.** The **official mercury compounds** and preparations include:

*Preparations of Metallic Mercury.*

Mercury with chalk; hydrargyrum cum creta. Grayish, insoluble powder.

Mercury with magnesia; hydrargyrum cum magnesia. Grayish, insoluble powder.

Mercury mass; massa hydrargyri. Commonly called "blue mass" or "blue pill." Light grayish-blue, softish solid.

Mercury ointment; unguentum hydrargyri. Blue ointment. Light, grayish-blue, medium soft ointment.

Mercury plaster; emplastrum hydrargyri. Light grayish-blue. Firm solid.

Ammoniac plaster with mercury; emplastrum ammoniaci cum hydrargyro. Grayish. Firm solid.

*Mercurous Compounds.*

Hg<sub>2</sub>O, Mercurous oxide; hydrargyri oxidum nigrum. Insoluble blackish powder.

HgCl, Mercurous chloride; hydrargyri chloridum mite. Mild chloride of mercury. Calomel. White, insoluble powder.

HgI, Mercurous iodide; hydrargyri iodidum flavum. Also called green iodide of mercury. Yellow or greenish-yellow, amorphous, insoluble powder.

HgNO<sub>2</sub>, Mercurous nitrate; hydrargyri mononitras. White or colorless, crystalline. Decomposed by water.

*Mercuric Compounds.*

HgO, Mercuric oxide; hydrargyri oxidum rubrum and hydrargyri oxidum flavum. Red oxide of mercury or red precipitate, and yellow oxide of mercury or precipitated mercuric oxide. Red oxide is granular, coarse, sometimes somewhat crystalline. Yellow oxide is an impalpable amorphous powder. Both are insoluble.

- $\text{HgCl}_2$ , Mercuric chloride; hydrargyri chloridum corrosivum. corrosive chloride of mercury. "Corrosive sublimate." Colorless or white crystals. Soluble.
- $\text{HgI}_2$ , Mercuric iodide; hydrargyri iodidum rubrum red iodide of mercury. A vermilion-colored powder, or minute scarlet crystals. Insoluble.
- $\text{HgBr}_2$ , Mercuric bromide; hydrargyri bromidum. White, crystalline. Soluble.
- $\text{HgCy}_2$ , Mercuric cyanide; hydrargyri cyanidum. White, crystalline. Soluble.
- $\text{HgS}$ , Mercuric sulphide; hydrargyri sulphidum rubrum, and hydrargyri sulphidum nigrum. Crystallized is red. Precipitated amorphous sulphide is black, but can be converted into a red powder called vermilion. Insoluble.
- $\text{HgNH}_2\text{Cl}$ , Mercurammonium chloride, or mercuric chloramide; hydrargyrum ammoniatum. Ammoniated mercury. "White precipitate." Insoluble, white powder.
- $\text{HgSO}_4$ , Mercuric sulphate; hydrargyri sulphas albus. White, crystalline. Decomposed by water.
- $\text{HgO}_2(\text{HgO})_2\text{SO}_2$ , Basic mercuric sulphate; hydrargyri sub-sulphas flavus. Lemon yellow, insoluble powder.

*Preparations of Mercuric Compounds.*

- Ointment of yellow mercuric oxide; unguentum hydrargyri oxidi flavi. A soft yellow ointment.
- Ointment of red oxide of mercury; unguentum hydrargyri oxidi rubri. A soft red ointment.
- Ointment of ammoniated mercury; unguentum hydrargyri ammoniati. A soft white ointment.
- Ointment of mercuric nitrate; unguentum hydrargyri nitratis. "Citrine ointment." Medium firm, lemon yellow or orange yellow.
- Solution of mercuric nitrate; liquor hydrargyri nitratis. Colorless.
- Oleate of mercury; hydrargyri oleatum. Yellowish brown, soft, ointment-like. Solid.

In addition to these mercury preparations several others are occasionally employed.

**721. Medicinal uses.** Mercury compounds administered internally are employed as alteratives, purgatives, etc.

Mercuric compounds are more active than mercurous compounds, and soluble mercury compounds are more active than the insoluble. Most of the mercuric and some mercurous compounds are quite poisonous.

Metallic mercury is not poisonous if pure.

The preparations of metallic mercury prescribed for internal use are, therefore, generally held to be entirely safe. But such preparations, unless perfectly fresh, are liable to contain oxides of mercury. The quantity of oxidized mercury in "blue mass" increases with its age, and an older preparation is often far more active than a fresher one. Mercury ointment is probably less liable to contain the oxides, and it is sometimes preferred to blue mass even for internal use; but as at present prepared the ointment can not be used internally, for one of the ingredients now ordered by the Pharmacopœia to be used in preparing mercury ointment is *oleate of mercury*.

*Mercuric cyanide* is the most poisonous of the mercury compounds, not only because it is a cyanide, but also because of its solubility. The *mercuric chloride* is next after the cyanide the most active and poisonous mercuric compound. Mercuric cyanide is fortunately very rarely used.

Calomel is quite insoluble in water; but it is not improbable that it forms soluble compounds by reaction with halides. Calomel, mercury with chalk, and mercurous iodide are the mercurials most frequently employed in the form of powder; both mercuric and mercurous chlorides and iodides are prescribed in pill form. The only mercury compounds employed in liquid form for internal administration are mercuric chloride which is soluble in water and in alcohol, and mercuric iodide dissolved in potassium iodide solution.

Mercurous compounds, when associated with oxidizing agents, are liable to be changed to mercuric.

**722.** Among the *symptoms of poisoning* by potent mercury compounds are the following:

Diuresis, pain and inflammation of the stomach and bowels, thirst, vomiting, salivation, weak and irregular pulse.

*Antidotes.*—The measures which may be adopted to prevent or counteract poisoning by corrosive sublimate or other mercur-

rials taken in quantities such as might prove dangerous or fatal, include: Evacuation of the stomach by emetics and copious draughts of tepid water; and, as chemical antidotes, sodium carbonate dissolved in plenty of water and milk, raw white of egg, or vegetable astringents.

**723. Reactions.** All mercury compounds, when mixed with dry sodium carbonate or calcium oxide and heated in a test-tube, produce a sublimate of metallic mercury. When a strip of clean bright copper is placed in a solution or mixture containing a mercury salt, a gray film of mercury is after a time deposited upon the copper, and this gray coating becomes silver-white when rubbed.

Solutions of *mercurous salts* give a precipitate of metallic mercury with stannous chloride; a black precipitate of mercurous oxide with KOH, NaOH, or  $\text{Ca}(\text{OH})_2$ ; a black mercurous chlor-amido-compound with ammonia; black mercurous sulphide with  $\text{H}_2\text{S}$ ; a white precipitate of calomel with HCl or NaCl; and a greenish-yellow or yellow mercurous iodide with KI.

Solutions of *mercuric salts* give with stannous chloride a precipitate of either calomel or metallic mercury; with KOH, yellow oxide; with ammonia a white mercuric chlor-amido-compound; with KI, red mercuric iodide; with  $\text{H}_2\text{S}$ , at first a white precipitate, which, on the addition of more of the reagent, changes to yellow, orange, and finally black, this precipitate being insoluble in nitric acid. Mercuric salts are not precipitated by HCl or NaCl.

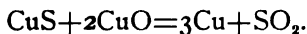
## CHAPTER L

### COPPER.

Symbol, Cu, At.w., 63.5.

**724. Occurrence and production.** Copper is found in large quantities uncombined with other elements, in the mines of the Lake Superior regions and elsewhere. It is also found in the form of sulphide, oxide, and carbonate. The natural copper sulphides are generally associated with sulphides of other metals, particularly iron. Copper pyrites,  $\text{CuFeS}_2$ , is a common copper ore.

The free copper of the Lake Superior mines is obtained by crushing the ore, reducing it to such a finely divided state that the mineral compounds can be washed away leaving the heavy copper, which is then fused and cast into bars or ingots. The sulphides of copper are crushed, roasted, to remove as much of the sulphur as practicable by oxidation to  $\text{SO}_2$ . A portion of the copper sulphide remains undecomposed while another portion is converted into oxide. Then the mixture of sulphide and oxide is heated in a reverberatory furnace, when copper and sulphur dioxide are formed:



But while this is the practical net result, the processes necessary to its accomplishment involve various reactions and separations descriptions of which would be out of place in a book of the scope of this volume.

**725. Description and chemical properties.** Copper is reddish; harder than silver or lead, but softer than iron; capable of high polish; malleable and ductile; not tarnished in pure, dry air. Its sp.w. is 8.9. It melts at about  $1090^\circ \text{C}$ .

Copper is attacked by solutions of the halides, such as sodium chloride. Ammonium chloride attacks it vigorously. Ammonia slowly dissolves copper.

Copper is measurably attacked by any of the common soluble

acids, organic or inorganic, but especially by nitric acid and by strong sulphuric acid. Hydrochloric acid and dilute sulphuric acid do not act rapidly upon copper.

**726. Uses.** Copper is the best conductor of electricity next after silver, and it is also an exceptionally good conductor of heat. Copper vessels, such as stills, pans, kettles, dishes, etc., are, therefore, much employed. Copper stills, of course, do not require tinning, and even evaporating pans and kettles may be safely used in many operations without any danger of contamination of the contents by copper compounds. But when organic substances are heated in untinned copper vessels while the air has free access to the contents there is danger that the copper will be attacked and the contents contaminated, especially if left in the vessel until cold. Fruit syrups and preserves may be heated in untinned copper or brass kettles without danger provided a considerable proportion of sugar is present and the syrup or preserves transferred to other vessels before cooling. But it is much safer not to use copper vessels for such purposes unless well tinned. Acetic acid attacks copper so that pickles should never be made in copper vessels.

*Brass* consists of about 7 parts of copper and 3 parts of zinc. The kind of brass employed for making weights has usually the sp.w. 8.3.

*Bronze* contains copper and tin.

**727. Compounds.** Copper acts as a monad in cuprous compounds and as a dyad in cupric compounds.

Copper compounds are blue, green, white, brown or black. When soluble they have a nauseous, strongly metallic or "brassy," persistent taste, and are poisonous. Their structure is illustrated by the following:

$\text{Cu}_2\text{O}$ , Cuprous oxide. Red solid. Insoluble.

$\text{CuO}$ , Cupric oxide. Black solid. Insoluble.

$\text{Cu}_2\text{S}$ , Cuprous sulphide. Amorphous, black powder. Insoluble.

$\text{CuS}$ , Cupric sulphide. Amorphous, insoluble, black powder.

$\text{Cu}_2\text{Cl}_2$ , Cuprous chloride. White, crystalline. Insoluble.

$\text{CuCl}_2$ , Cupric chloride. Green, crystalline. Soluble.

$\text{Cu}(\text{OH})_2$ , Cupric hydroxide. Green, insoluble, amorphous powder.

$\text{Cu}(\text{NO}_3)_2$ , Cupric nitrate. Blue crystals. Soluble.

$\text{CuSO}_4$ , Cupric sulphate; anhydrous. White. Soluble with blue color.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , Crystallized cupric sulphate. Blue crystals. Soluble.

$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ , Cupric acetate. Dark green, crystalline. Soluble.

Many copper compounds are soluble in ammonia water, the solutions having a beautiful blue color.

Sulphate, nitrate and acetate of copper, and "ammoniated copper" are officinal.

*Copper sulphate* is manufactured upon a very extensive scale by the treatment of roasted copper sulphide ores with water in free access of air, and by dissolving copper in strong sulphuric acid. Other copper compounds are most frequently made from the sulphate.

**728. Reactions.** Copper compounds in solution give black precipitates with  $\text{H}_2\text{S}$  and with  $\text{H}_4\text{NSH}$ ; they strike a blue color with ammonia in excess, and this color is perceptible even in extremely dilute solutions. *Cupric salts* give blue precipitates with  $\text{KOH}$  or with  $\text{K}_2\text{CO}_3$ , and brown precipitates with  $\text{K}_4\text{Fe}(\text{CN})_6$ . With  $\text{KOH}$  *in excess* the cupric salts give no precipitate but a blue liquid instead *if sugar or tartaric acid be present* in sufficient quantity. *Cuprous salts* give a yellow precipitate with  $\text{KOH}$ .

Iron and zinc precipitate metallic copper from acidulated solutions of all copper salts. If a bright clear iron nail, piece of iron wire, or other bright piece of that metal, be inserted in a solution or mixture containing any copper compound in solution, the iron will soon be coated with a reddish deposit of metallic copper. This will impart a blue color to ammonia water.

All copper compounds color the edge of a flame (the Bunsen burner, blow-pipe, or other flame) green. To the borax bead they impart in the outer or oxidation flame a green color, and in the inner or reduction flame a brown red color.

## CHAPTER LI.

### LEAD.

Symbol, Pb, At.w., 206.5.

**729. Occurrence and production.** Lead occurs chiefly in the form of sulphide, PbS, as *galena* or lead ore.

The ore is heated in a reverberatory furnace when oxide and sulphate are first formed and these then react with another portion of the sulphide, so that metallic lead and sulphur dioxide are the final products:

1.  $\text{PbS} + 3\text{O} = \text{PbO} + \text{SO}_2.$
2.  $\text{PbS} + 4\text{O} = \text{PbSO}_4.$
3.  $\text{PbS} + 2\text{PbO} = 3\text{Pb} + \text{SO}_2.$
4.  $\text{PbS} + \text{PbSO}_4 = 2\text{Pb} + 2\text{SO}_2.$

**730. Description.** Lead is soft gray or bluish-white. It has a bright metallic luster when freshly cut or scraped, but tarnishes rapidly in the air. It is malleable. The sp. w. is 11.4, and its melting point  $330^\circ \text{C}$ . It boils at white heat.

Lead is rapidly dissolved by nitric acid. It is also acted upon energetically by acetic acid. Hydrochloric acid acts upon lead only slightly, and cold sulphuric acid of moderate strength does not affect it, while concentrated sulphuric acid, especially if hot, dissolves an appreciable amount as sulphate.

**731. Compounds.** Lead in its most common and stable compounds acts as a dyad; but it is also capable of acting as a tetrad. The principal *oxide* of lead is PbO, which occurs as red "litharge" and yellow "massicot." So-called "red lead" or *minium* is a combination of 2PbO and PbO<sub>2</sub>, usually represented as Pb<sub>3</sub>O<sub>4</sub>. Lead peroxide is PbO<sub>2</sub>, which is frequently employed as an oxidizing agent, being reduced to PbO when heated.

The compounds of lead are white, colorless, lemon yellow, reddish yellow, bright red, or black. Soluble lead salts have a nauseous, sweetish-astringent, metallic taste.

The only readily water-soluble lead salts are the nitrate and acetate. The chloride,  $\text{PbCl}_2$ , is so sparingly taken up by water as to be described as practically insoluble; but it is soluble enough to poison drinking water when the water contains any chlorides and is allowed to pass through lead pipes a great distance or to be in contact with lead a long time.

Lead oxide is the most readily available material for the preparation of the nitrate and acetate; and these in turn are employed for preparing many of the insoluble lead compounds by precipitation.

**732.** The official lead preparations include:

$\text{PbO}$ , Lead oxide; plumbi oxidum. Red or yellow. Insoluble.  
 $\text{PbI}_2$ , Lead iodide; plumbi iodidum. Lemon yellow. Insoluble.  
 $\text{Pb}(\text{NO}_3)_2$ , Lead nitrate; plumbi nitras. White or colorless. Soluble.

$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , Lead acetate; plumbi acetas. Called also "sugar of lead." Colorless or white. Soluble.

$\text{Pb}(\text{OH})\text{C}_2\text{H}_3\text{O}_2$ , Lead subacetate; plumbi subacetas. White. Soluble.

$\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ , "Lead carbonate;" plumbi carbonas. Formerly called "cerussa." White. Insoluble powder.

"White lead," so extensively employed in paints, is also a basic lead carbonate.

All lead compounds are more or less poisonous.

Lead acetate is much more frequently employed for medicinal purposes than all the other lead compounds together.

**733. Reactions.** Lead compounds, when mixed with dry sodium carbonate and heated upon charcoal before the blow pipe, produce a bead of metallic lead, and around it a reddish-yellow film of lead oxide.

Soluble lead salts in solution give a black precipitate with  $\text{H}_2\text{S}$ ; with  $\text{KOH}$  they afford a white precipitate soluble in an excess of the reagent, but insoluble in ammonia; they give a white precipitate with sulphuric acid and other sulphates, and white precipitates also with the carbonates, phosphates, oxalates, and chlorides; a yellow precipitate is formed with potassium iodide.

Iron and zinc precipitate the lead from solutions containing lead salts.

## CHAPTER LII.

### MANGANESE.

Symbol, Mn, At.w., 55.

**734. Occurrence and production.** Manganese occurs in nature combined with oxygen in the minerals: *Pyrolusite*,  $\text{MnO}_2$ ; *braunite*,  $\text{Mn}_2\text{O}_3$ ; *hausmannite*,  $\text{Mn}_3\text{O}_4$ ; and *manganite*,  $\text{MnO}(\text{OH})$ .

It is produced by reduction of the ores with carbon in a blast furnace at a very high temperature.

**735. Description.** Manganese is a very hard, brittle, difficultly fusible metal. It oxidizes readily in moist air, and decomposes water at the boiling point. Its sp. w. is about 7.5. It is soluble in dilute acids.

Manganese forms five different oxides. When it performs basic functions it has a polarity-value of +2; in the manganates its polarity-value is +6, and permanganates +7. The manganates accordingly correspond in structure to the sulphates, and the permanganates to the perchlorates.

**736.** The following table of manganese compounds exemplifies the structure of the most important of them:

$\text{MnO}$ , Manganous oxide. Greenish or gray. Insoluble.

$\text{Mn}_2\text{O}_3$ , Manganic oxide. Brown. Insoluble.

$\text{MnO}_2$ , Manganese dioxide; mangani dioxidum. Brownish black. Insoluble.

$\text{MnO}_3$ , Manganese trioxide.

$\text{Mn}_2\text{O}_7$ , Manganese heptoxide.

$\text{MnCl}_2$ , Manganous chloride. Pale red. Soluble.

$\text{MnSO}_4$ , Manganous sulphate; mangani sulphas. Pale red, crystalline. Soluble.

$\text{K}_2\text{MnO}_4$ , Potassium manganate. Brown. Soluble.

$\text{KMnO}_4$ , Potassium permanganate; potassii permanganas. Dark purple, crystalline. Soluble.

Compounds of manganese and of chromium present many analogies.

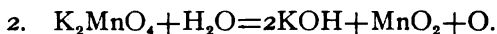
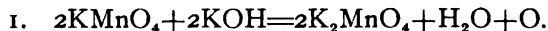
Manganous salts and manganous sulphide are of a pink or salmon color, pale rose color, or white.

Manganese dioxide,  $\text{MnO}_2$ , is employed as an oxidizing agent in the preparation of various substances, as, for instance, in the production of chlorine and of potassium manganate and permanganate. It is also used in preparing oxygen from potassium chlorate.

Potassium permanganate is a very powerful oxidizing agent. In *acid* solutions the permanganate is reduced to manganous salt:



In *alkaline* solutions the oxidation with permanganate results in its reduction to manganate and then to dioxide:



Manganese dioxide, manganous sulphate and potassium permanganate are officinal.

**737. Reactions.** Solutions of manganous salts give white precipitates with  $\text{KOH}$ ; the color of these precipitates changes to brown by oxidation in contact with the air. Ammonia also precipitates white manganous hydroxide, which turns brown; but if a sufficient quantity of an ammonium salt be present no precipitate will be formed on the addition of  $\text{H}_3\text{N}$ , so that an *acid* solution of a manganous salt gives no precipitate with ammonia. Alkali carbonates and phosphates produce white or pale-rose-colored precipitates; potassium ferrocyanide a reddish-white one; and  $(\text{H}_4\text{N})_2\text{S}$  produces a salmon-colored precipitate of manganous sulphide. Manganous salts do not give any precipitate with  $\text{H}_2\text{S}$ .

Fused with sodium carbonate the manganese compounds form a bluish-green flux. They produce a violet-colored blow-pipe bead in the outer flame.

## CHAPTER LIII.

### CHROMIUM.

Symbol, Cr, At.w., 52.

**738. Occurrence and production.** Chromium occurs combined in the "chrome iron ore," which is  $\text{Cr}_2\text{FeO}_4$ , and in "chrome ore,"  $\text{Cr}_2\text{O}_3$ .

It is produced by reducing the oxide with carbon, or by treating the chloride with metallic sodium.

The metal is obtained only in the form of a hard, gray, crystalline powder, or in small crystals. Its sp. w. is 7.3. It is infusible.

Chromium is not attacked by nitric acid, but forms chloride with HCl.

**739.** In many respects the chromium compounds resemble in structure those of the iron group of metals, but the chromates are analogous to the sulphates for acidic chromium has a polarity-value of +6.

The chromates and chromic anhydride are oxidizing agents.

Reducing agents convert chromates into salts of basic chromium, while chromous compounds form chromic salts in the presence of acids, and chromates in the presence of strong bases.

The following illustrations of the structure of chromium compounds will suffice:

$\text{CrCl}_2$ , Chromous chloride. A white solid, forming a blue solution in water.

$\text{Cr}(\text{OH})_2$ , Chromous hydroxide. A brown insoluble powder.

$\text{Cr}_2\text{O}_3$ , Chromic oxide. A green infusible and insoluble powder.

$\text{Cr}(\text{OH})_3$ , Chromic hydroxide. A grayish-blue, or greenish-gray precipitate.

$\text{CrCl}_3$ , Chromic chloride. Light-violet scales; or a green salt-mass. Soluble in water.

$\text{Cr}_2(\text{SO}_4)_3$ , Chromic sulphate. Purple crystals forming a blue solution in water, which turns green when boiled.

- $\text{CrO}_3$ , Chromic anhydride. Commonly called "chromic acid" (acidum chromicum) even in the pharmacopœias. A dark red crystalline solid substance. Readily soluble in water.
- $\text{K}_2\text{CrO}_4$ , Potassium chromate. A pale yellow, crystalline water-soluble salt.
- $\text{K}_2\text{Cr}_2\text{O}_7$ , Potassium dichromate; potassii dichromas (or bichromas). Orange-red crystals. Soluble in water.
- $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , Chrome alum. Purple crystals. Readily soluble.

Chromic anhydride and potassium dichromate are officinal.

**740. Identification.** The chromium compounds are blue, green, purple, red or yellow.

Chromic salts, when hydrous, are bluish or green, and, when soluble, have an acid reaction. They give a bluish-gray or grayish-green precipitate of chromic hydroxide with  $\text{H}_3\text{N}$  or with  $\text{H}_4\text{NSH}$ ;  $\text{KOH}$  produces a similar precipitate, soluble in an excess of that precipitant with green color, but reprecipitated on boiling the liquid. Chromic salts give no precipitate with  $\text{H}_2\text{S}$ . When fused with potassium nitrate the chromic salts produce a yellow mass containing potassium chromate which imparts a yellow color to water.

Chromates are yellow or red. When  $\text{H}_2\text{S}$  is introduced into their solutions, sulphur is precipitated and  $\text{Cr}_2\text{O}_3$  is formed, which is also thrown down; but if the liquid contains a sufficiency of free acid no precipitate is formed, but a green solution containing chromic salt.

Chromium compounds give green borax beads before the blow-pipe flame.

## CHAPTER LIV.

### IRON.

Symbol, Fe. At.w., 56.

**741. Occurrence and production.** Iron occurs in nature in the form of oxides, hydroxides, carbonates and sulphides, and in many other compounds. The sulphur compounds, called "iron pyrites," are very abundant; but the workable iron ores do not include the sulphides.

The best iron ore is "magnetic iron ore,"  $\text{Fe}_3\text{O}_4$ .

Iron ores are reduced to metallic iron by means of carbon at very high temperatures in blast furnaces.

**742. Description.** Iron occurs in three distinct forms in commerce. These several forms of metallic iron differ very materially from each other in their physical properties. They are: "Wrought iron," "steel," and "cast iron." All contain carbon and minute quantities of other elements. Each kind has its own distinct uses, and one can not take the place of another.

*Wrought iron* contains the greatest proportion of pure iron and the smallest proportion of carbon. It is tenacious and malleable and can be forged.

*Steel* contains a somewhat larger quantity of carbon. Other metals are frequently added to steel to impart to it certain desirable qualities. The metals so used are manganese, tungsten and chromium. Steel can be "tempered" or hardened. The tenacity of certain kinds of steel is very great, and its employment in the manufacture of edge tools and other tools, and rails, plate, machinery, and "structural iron," depends upon its hardness and tenacity. Steel can be forged.

*Cast iron* contains much more carbon and is brittle. But it is suitable for certain kinds of castings. Cast iron can not be forged.

The softest wrought iron, such as is used for the manufacture of wire, is nearly pure iron and can be used for the production of chemical and pharmaceutical preparations.

The pharmacopœias usually prescribe "fine, bright, non-elastic wire."

"Reduced iron" is perfectly pure, finely divided iron.

"Powdered iron" is also employed in medicine, and prescribed in some pharmacopœias.

*Pure iron* in mass is slightly softer than wrought iron. Its sp. w. is from 7.3 to 7.9. It melts at about  $2000^{\circ}$  C.

The ordinary acids attack iron most readily when they are moderately diluted. Concentrated nitric acid does not dissolve iron, but dilute nitric acid attacks it vigorously.

**743. Compounds.** Iron is a dyad in ferrous compounds and a triad in ferric compounds.

The general structure of ferrous and ferric compounds is shown in the following examples:

$\text{FeO}$ , Ferrous oxide.

$\text{FeS}$ , Ferrous sulphide.

$\text{FeCl}_2$ , Ferrous chloride ( $\text{Fe}_2\text{Cl}_4$  at low temperatures).

$\text{FeBr}_2$ , Ferrous bromide.

$\text{FeI}_2$ , Ferrous iodide.

$\text{Fe}(\text{OH})_2$ , Ferrous hydroxide.

$\text{FeCO}_3$ , Ferrous carbonate.

$\text{FeSO}_4$ , Ferrous sulphate ( $\text{FeH}_2\text{SO}_5$ ).

$\text{FeC}_2\text{O}_4$ , Ferrous oxalate.

$\text{Fe}_2\text{O}_3$ , Ferric oxide.

$\text{FeCl}_3$ , Ferric chloride (at above  $700^{\circ}$ ;  $\text{Fe}_2\text{Cl}_6$  at  $448^{\circ}$ ).

$\text{Fe}(\text{OH})_3$ , Ferric hydroxide.

$\text{Fe}_2\text{S}_3$ , Ferric sulphide.

$\text{Fe}(\text{NO}_3)_3$ , Ferric nitrate.

$\text{Fe}_2(\text{SO}_4)_3$ , Ferric sulphate.

$\text{Fe}_3(\text{PO}_4)_2$ , Ferric phosphate.

All soluble iron compounds have an acid reaction on test-paper.

**744.** The colors of iron compounds. *Ferrous compounds*, when hydrous or in water-solution, are generally green or greenish-blue; when dry they are generally white or grayish-white. But the sulphide is black, the oxalate sulphur yellow, and the lactate light greenish-yellow. Solutions of ferrous salts, in the presence of much sugar, are slowly decolorized or nearly so when exposed to light, and the sugar at the same time becomes inverted. Syrup

of ferrous iodide soon becomes nearly colorless when exposed to strong light.

When an alkali (KOH, NaOH, or  $H_4NOH$ ) is added to a solution of a ferrous salt containing much sugar, no precipitation results, but the green color of the solution is decidedly deepened.

*Ferric compounds*, when hydrous or in water solution, are generally reddish-brown; but when dry they are most frequently pale yellow or nearly white. But ferric sulphide is black, and ferric oxide and hydroxide are red.

Tincture of ferric chloride is reddish-brown, but becomes lighter on exposure to light, and finally pale reddish-yellow if long kept in direct sunlight.

A solution of ferric chloride mixed with much syrup is not precipitated by an alkali (KOH, NaOH, or  $H_4NOH$ ), but its brown color is materially deepened.

Several brown-red or reddish-brown ferric salts are rendered green or greenish by the alkali citrates. Ferric hypophosphite also forms a green solution with sodium citrate.

*Ferroso-ferric compounds* are compounds containing both ferrous and ferric iron. Their colors frequently differ surprisingly from both ferrous and ferric compounds. Ferroso-ferric hydroxide is nearly black, although ferrous hydroxide is nearly white and ferric hydroxide red-brown. Ferric ferrocyanide containing water, called "prussian blue," has a rich, dark blue color; but anhydrous ferric ferrocyanide is white. Ferrous phosphate and ferric phosphate are both nearly white; but ferrous phosphate containing also ferric phosphate is grayish-blue.

**745.** The **taste** of iron compounds. Water-soluble iron compounds unless associated with certain organic substances usually have a peculiar, disagreeable "inky" or "chalybeate" astringent ferruginous taste. This taste is in many cases, especially in ferric salts, overcome by the addition of alkali citrates and tartrates. "Scale-salts" of iron do not possess that inky astringent taste.

**746.** **Solubilities of iron compounds.** The oxides, hydroxides, sulphides, carbonates, oxalates, phosphates, hypophosphites, salicylates and oleates of iron are insoluble in water.

But certain iron compounds which are insoluble in water are rendered soluble by combination with sugar, albumin, citrates, tartrates, glycerin or other substances. Thus we have water-soluble "saccharated oxide of iron," "albuminated iron," phos-

phate, pyrophosphate, and hypophosphite of iron, tartrate of iron and potassium, tartrate of iron and ammonium, etc.

**747. Basic iron compounds** are common. There are several ferric meta-hydroxides. The water-solutions of several ferric salts, as the chloride, nitrate, sulphate and acetate, dissolve large proportions of freshly precipitated ferric hydroxide. "Dialysed Iron" and Solution of Basic Ferric Sulphate are examples of officinal preparations containing such compounds.

**748.** The principal **materials** employed for the production of iron compounds are: metallic iron, ferrous sulphate, ferric hydroxide, ferric sulphate and ferric chloride.

*Water-soluble ferrous salts* are frequently made by dissolving metallic iron, in the form of wire ("card teeth" are much used) or reduced iron, in the requisite acids, the acid being completely saturated with iron. Ferrous sulphate, ferrous phosphate, ferrous lactate and ferrous chloride may be so made.

*Insoluble ferrous compounds* are generally made from ferrous sulphate by metathesis.

*Water-soluble ferric salts* are very frequently made by dissolving ferric hydroxide in the requisite acid; but ferric sulphates and ferric chloride are generally prepared by the oxidation of the corresponding ferrous compounds.

*Insoluble ferric compounds* are produced by metathesis, from ferric chloride or ferric sulphate.

**749.** The **officinal iron compounds** and preparations are very numerous. They include:

Powdered Iron; Ferrum Pulveratum.

Reduced Iron; Ferrum Reductum.

### *Ferrous Compounds.*

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , Ferrous chloride; ferri chloridum viride. Pale green crystals. Soluble.

$\text{FeBr}_2$ , Ferrous bromide; ferri bromidum. Used in the form of a syrup. Green.

$\text{FeI}_2$ , Ferrous iodide; ferri iodidum. Used in the form of saccharated iodide of iron and syrup of ferrous iodide. Ferrous iodide is green and readily soluble. Pills of iodide of iron are also officinal.

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , or rather  $\text{FeH}_2\text{SO}_6 \cdot 6\text{H}_2\text{O}$ , Ferrous sulphate; ferri sulphas. Bluish-green, crystalline. Readily soluble. This is used in large crystals as well as in crystalline granular form, obtained by turbidation or by precipitation.

$\text{FeH}_2\text{SO}_6$ , Dried ferrous sulphate; ferri sulphas exsiccatus. Nearly white; powder; slowly soluble.

$\text{Fe}_3(\text{PO}_4)_2$ , Ferrous phosphate. Used in the form of syrup. Pale green; insoluble in water, but soluble in dilute phosphoric acid.

$\text{FeCO}_3$ , Ferrous carbonate; ferri carbonas. Greenish-gray powder; insoluble. Used in the form of saccharated ferrous carbonate, mass of ferrous carbonate, and pills. Also contained in Compound Iron Mixture.

$\text{FeC}_2\text{O}_4$ , Ferrous oxalate; ferri oxalas. Sulphur-yellow powder. Insoluble.

$\text{Fe}(\text{C}_3\text{H}_5\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$ , Ferrous lactate; ferri lactas. Pale greenish-yellow or nearly white powder. Soluble.

#### *Ferric Compounds.*

$\text{Fe}_2\text{O}_3$ , Ferric oxide; ferri oxidum. Used in various forms. The "subcarbonate of iron" is largely  $\text{Fe}_2\text{O}_3$  mixed with a very basic ferric meta-hydroxide. Red-brown. Insoluble.

$\text{Fe}(\text{OH})_3$ , Ferric hydroxide; ferri hydroxidum. Called "ferri oxidum hydratum" in the Pharmacopœia. Red-brown, amorphous, insoluble. This compound is also an important constituent in the "Antidote for Arsenic," called ferri oxidum hydratum cum magnesia.

$\text{FeCl}_3$ , Ferric chloride; ferri chloridum. Crystalline, orange-yellow masses. Hygroscopic. Extremely freely soluble. Employed in the solid state, in water-solution, and in the form of tincture of ferric chloride. Ferric chloride is still frequently called "sesquichloride of iron," "perchloride of iron," and even "muriate of iron."

$\text{Fe}(\text{NO}_3)_3$ , Ferric nitrate; ferri nitras. Used in solution, which is reddish; liquor ferri nitratis. Also called "liquor ferri pernitratis" (Br.).

$\text{Fe}_2(\text{SO}_4)_3$ , Ferric sulphate; ferri tersulphas. Used in solution, which is red-brown. Liquor ferri tersulphatis. Also called "solution of persulphate of iron" (Br.).

$\text{Fe}_4\text{O}(\text{SO}_4)_6$ , Ferric subsulphate; ferri subsulphas. A lemon-yellow or orange-yellow powder. Hygroscopic and extremely readily soluble. The Pharmacopœia contains a red-brown "solution of subsulphate of iron;" liquor ferri subsulphatis. This is also called "Monse's solution."

$\text{FeH}_4\text{N}(\text{SO}_4)_4 \cdot 12\text{H}_2\text{O}$ , Ammonio-ferric alum, or iron alum; ferri et ammonii sulphas. Purple, violet, or rose-colored crystals. Freely soluble.

$\text{FePO}_4$ , Ferric phosphate; ferri phosphas. A nearly white amorphous, insoluble powder. "Soluble phosphate of iron," ferri phosphas solubilis, is ferric phosphate combined with sodium citrate. This consists of greenish, or brownish-green, freely soluble scales.

$\text{Fe}_4(\text{P}_2\text{O}_7)_3$ , Ferric pyrophosphate; ferri pyrophosphas. A nearly white, amorphous, insoluble powder. Contained in the soluble pyrophosphate of iron of the Pharmacopœia; ferri pyrophosphas solubilis. This is a combination of ferric pyrophosphate with sodium citrate and consists of green or brownish-green readily soluble scales.

$\text{Fe}(\text{PH}_2\text{O}_2)_3$ , Ferric hypophosphite; ferri hypophosphis. A grayish-white powder. Nearly insoluble in water.

$\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$ , Ferric acetate; ferri acetas. A brown-red or red salt easily soluble. Used in the form of the red liquor ferri acetatis, and the tinctura ferri acetatis made from the solution. It is also contained in the mistura ferri et ammonii acetatis.

#### *Ferric Compounds of Indefinite Composition.*

Iron and potassium tartrate; ferri et potassii tartras. Garnet red to red-brown scales. Freely soluble.

Iron and Ammonium tartrate; ferri et ammonii tartras. Garnet red to red-brown; freely soluble scales.

Ferric citrate; *ferri citras*. Garnet red, slowly but perfectly soluble scales. Also used in the form of the red-brown solution *liquor ferri citratis*.

Iron and ammonium citrate; *ferri et ammonii citras*. Garnet red, freely soluble scales.

Iron and quinine citrate; *ferri et quininæ citras*. Brown-red scales, slowly but completely soluble.

Soluble iron and quinine citrate; *ferri et quininæ citras solubilis*. Greenish or golden-yellow, readily soluble scales.

Iron and strychnine citrate; *ferri et strychninæ citras*. Garnet to yellowish-brown scales. Readily soluble.

Ferric oleate; *ferri oleatum*. A red-brown plaster-like solid.

Saccharated oxide of iron; *ferri oxidum saccharatum solubile*. A chocolate-brown, readily soluble powder.

Troches, pills, wines, plaster, and other preparations containing iron are also official.

**750. Uses and behavior.** The iron preparations are chiefly employed as tonics; but some of the water-soluble salts, as the ferric sulphate, ferric subsulphate, ferric nitrate, and ferric chloride, are used as astringents, styptics and hæmostatics.

The preparations most frequently employed for internal administration are probably: reduced iron and dried ferrous sulphate in pills, and the pills of carbonate of iron; of the liquid preparations the tincture of ferric chloride is the most important. But syrup of ferrous iodide, the "scale salts" of iron, and several other compounds are much used.

All water-soluble iron salts form inky and turbid mixtures with vegetable extracts, such as the tinctures and fluid extracts, because nearly all such preparations contain tannin with which iron forms insoluble dark-colored compounds. Even the "scale salts of iron" make dark mixtures and precipitates with vegetable extractive. Liquid preparations containing scale salts of iron must be carefully protected against light, because various changes in those compounds are always induced by it, especially if the liquids contain vegetable substances of any kind associated with the iron preparations. Such solutions may long remain unaltered in the dark, but become greatly changed on exposure to light, acquiring a darker or even blackish color and a disagreeable, inky taste, while at the same time insoluble matter is formed. Sometimes a curious succession of color changes may be observed

in elixirs and wines of ferric scale salts associated with alkaloids, the preparation becoming lighter and then darker, and again lighter and darker, alternately, but finally almost as black as ink. The shades of color usually to be observed in such liquid preparations when exposed to strong light are yellowish-red, greenish, yellow, reddish-brown, smoky-brown, and nearly bluish-black. While the presence of ammonium citrate or sodium citrate retards and minimizes these changes, nothing can wholly prevent them if the preparation is exposed to light. The soluble phosphate and pyrophosphate of iron seem to be far more sensitive to light than other scale salts. The phosphate is apparently less prone to change than the pyrophosphate in liquid preparations; but the most stable and satisfactory of the scale salts is the citrate of iron and ammonium.

Tartrate of iron and ammonium is much to be preferred to the tartrate of iron and potassium, for the former is more readily and completely soluble, more permanent, and less liable to form precipitates in mixtures. The tartrate of iron and potassium should not be prescribed in combination with any other medicinal agent if a clear solution is expected unless experience has demonstrated that the particular combination desired is practicable.

**751. Reactions of iron compounds.** Solutions of *ferrous compounds* afford white or greenish-gray precipitates with the alkalis. Such solutions are darkened but not immediately precipitated by tannin. They give a black precipitate with  $H_4NSH$ ; a deep blue precipitate with potassium ferrocyanide; with potassium ferricyanide they afford a bluish-white precipitate which soon turns blue in contact with the air; they do not give any precipitate with  $H_2S$ . Ferrous salts strike a dark-brown color with  $NO$ . Nitric acid, chlorine and other oxidizing agents rapidly convert ferrous compounds to ferric, and most of the ferrous salts change gradually to ferric on exposure to air.

Solutions of *ferric compounds* give red-brown precipitates with the alkalies and alkali carbonates; bluish-black precipitates with tannin; greenish-black with  $H_4NSH$ ; no precipitate with potassium ferricyanide; a blue precipitate with potassium ferrocyanide. Ferric salts are reduced to ferrous by  $H_2S$ , while sulphur precipitates; they are also reduced by  $SO_2$ ; or by being heated with iron or zinc.

But iron salts may not be precipitated by alkalies in the presence of sugar, glycerin, or albumin, or of citric or tartaric acid.

## CHAPTER LV.

### NICKEL AND COBALT.

**752. Nickel**, Ni, at.w. 58.5, occurs combined with arsenic and sulphur. Cobalt and nickel ores generally accompany each other. The principal nickel ore is the so-called "kupfernickel," NiAs, or nickelic arsenide. This is roasted to expel arsenic, after which the residue is digested with hydrochloric acid. The solution is treated with chlorinated lime and calcium hydroxide to remove iron and arsenic; the copper and other foreign metals are precipitated with  $\text{H}_2\text{S}$ , leaving nickel and cobalt in solution. This is again treated with chlorinated lime and heated, when the cobalt is separated. The clear solution is then treated with milk of lime ( $\text{Ca}(\text{OH})_2$  suspended in water), which throws down nickelous hydroxide,  $\text{Ni}(\text{OH})_2$ , which is reduced with charcoal at white heat to metallic nickel.

Nickel is a hard silver-white, tough metal, capable of high polish. Its sp. w. is 8.9. It fuses more readily than iron. It is not oxidized in dry air at common temperatures, and but slowly and slightly in moist air even when heated.

Nickel is slowly attacked by hydrochloric or sulphuric acid; rapidly by nitric acid.

This metal is used for electroplating iron and steel, and it also enters into certain useful alloys. Nickel coin is made of an alloy of 1 part of nickel and 3 parts of copper. "German silver" consists of 1 part of nickel, 3 parts of copper, and  $1\frac{1}{2}$  parts of zinc.

Nickel plated balances, weights, spatulas, and other instruments are much used.

**753. The compounds of nickel** are of two series, nickelous and nickelic, as shown by the following examples:

$\text{NiO}$ , Nickelous oxide.

$\text{Ni}_2\text{O}_3$ , Nickelic oxide.

$\text{Ni}(\text{OH})_2$ , Nickelous hydroxide; green, insoluble powder.

$\text{Ni}(\text{OH})_3$ , Nickelic hydroxide; black, insoluble powder.

$\text{NiCl}_2$ , Nickelous chloride; green, crystalline; soluble.

NiS, Nickelous sulphide; black, insoluble powder.

NiAs, Nickelic arsenide.

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ , (or  $\text{NiH}_2\text{SO}_6 \cdot 6\text{H}_2\text{O}?$ ), Nickelous sulphate;  
green, crystalline, soluble.

The most common nickel compounds are nickelous, which are generally formed, rather than nickelic compounds. When nickelic oxide is dissolved in sulphuric acid it forms nickelous sulphate.

Nickel compounds when hydrous are usually green or greenish-blue; anhydrous or dry salts are yellow. The soluble salts have an acid reaction.

**754. Reactions.** Acid solutions of nickelous salts with the stronger acids are not precipitated by  $\text{H}_2\text{S}$ ; but  $\text{H}_4\text{NSH}$  precipitates black NiS from alkaline or neutral solutions. Ammonia in excess produces no precipitate, but colors the solution of the nickelous salt blue. Potassium hydroxide precipitates green nickelous hydroxide from an alkaline or neutral solution.

Before the blow-pipe a reddish bead is formed by nickel in the outer flame, but the color almost disappears on cooling; in the inner flame the nickel compounds give a metallic button when heated on charcoal.

**755. Cobalt,** Co, at.w. 59., is not abundant. It generally accompanies nickel and is found combined with arsenic or sulphur, or both, and with iron. It is separated from the ores by methods similar to those by which nickel is produced. The cobalt hydroxide obtained from the ore is converted into  $\text{Co}_2\text{O}_3$ , which is then reduced to metal by heating it in a current of hydrogen. Cobalt can also be obtained by heating its oxalate.

Cobalt is a whitish, hard, lustrous metal, which fuses with difficulty. Its sp. w. is 8.9. Like nickel, it is readily soluble in nitric acid, but only very slowly acted upon by hydrochloric acid or sulphuric acid.

**756. The compounds of cobalt** are analogous to those of nickel and iron:

$\text{CoO}$ , Cobaltous oxide.

$\text{Co}_2\text{O}_3$ , Cobaltic oxide.

$\text{CoCl}_2$ , Cobaltous chloride.

$\text{CoCl}_3$ , Cobaltic chloride.

$\text{Co}(\text{OH})_2$ , Cobaltous hydroxide.

$\text{Co}(\text{OH})_3$ , Cobaltic hydroxide.

$\text{CoS}$ , Cobaltous sulphide.

$\text{Co}_2\text{S}_3$ , Cobaltic sulphide.

$\text{Co}(\text{NO}_3)_2$ , Cobaltous nitrate.

Cobaltous salts are more stable than the cobaltic. The cobaltous nitrate is used as a blow-pipe reagent.

A dilute solution of cobaltous chloride is called "sympathetic ink;" the writing produced with it is invisible until warmed.

Cobaltous salts are deliquescent. They have a beautiful red color when hydrous; the anhydrous salts are blue. The soluble salts have an acid reaction.

**757. Reactions.** Cobaltous salts afford a black precipitate of  $\text{CoS}$  with  $\text{H}_4\text{NSH}$ ; but no precipitate with  $\text{H}_2\text{S}$  unless they are the salts of comparatively weak acids. Acetate of cobalt is precipitated by  $\text{H}_2\text{S}$ , and hence a solution of any cobaltous salt affords a precipitate with  $\text{H}_2\text{S}$  if potassium acetate be added to the liquid. Bluish-red or light red precipitates are formed in the solutions of cobaltous salts by  $\text{KOH}$  or by  $\text{K}_2\text{CO}_3$ ; but in the presence of an ammonium salt no precipitate is obtained on the addition of  $\text{KOH}$  or  $\text{H}_4\text{NOH}$  to solutions of cobaltous compounds.

Cobalt compounds color the blow-pipe bead blue.

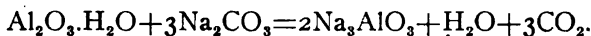
## CHAPTER LVI.

### ALUMINUM.

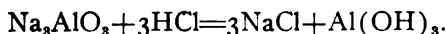
Symbol, Al, At.w. 27.

**758. Occurrence.** Aluminum occurs in nature in great abundance in combination with oxygen and silicon. *Clay* consists of aluminum silicate. The minerals *cryolite*,  $3\text{NaF}.\text{AlF}_3$ , and *beauxite*,  $\text{Al}_2\text{O}_3.\text{H}_2\text{O}$ , are common. Aluminum oxide, commonly called "alumina," exists in the forms known as emery, corundum, sapphire, and ruby. The double silicates called feldspar and mica also contain aluminum. Feldspar is  $\text{KAlSi}_3\text{O}_8$ ; mica is a complex mineral consisting of orthosilicates of aluminum, iron, magnesium and potassium.

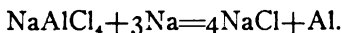
**759. Production.** The old process of producing aluminum was as follows: *Beauxite* was first converted into sodium aluminate by heating it with sodium carbonate:



A water-solution of the sodium aluminate is then treated with hydrochloric acid, which precipitates aluminum hydroxide, leaving sodium chloride in the liquid:



The aluminum hydroxide is mixed with sodium chloride and charcoal, and the intimate mixture is well dried and then heated in cylinders through which dry chlorine is passed. A double chloride of sodium and aluminum is formed, which distills over. This is mixed with metallic sodium and a flux of cryolite or fluor spar is added. When this mixture is heated in a reverberatory furnace the aluminum separates in a fused condition under the slag:



But aluminum is at present produced much more cheaply by elec-

trolysis. Aluminum oxide is first made from beauxite or some other aluminum compound. From beauxite it can be made by ignition. The oxide in a powdered state is dissolved in melted cryolite contained in a carbon-lined iron tank. Carbon cylinders are suspended in the molten mass and powerful currents of electricity are passed through the cylinders. Fused aluminum is then separated at the cathode (the negative electrode), while the oxygen from the decomposed aluminum oxide passes to the carbon anodes (the positive electrodes) which are soon consumed by combustion in the oxygen.

**760. Description.** Aluminum is a silver-white metal, malleable and ductile, capable of high polish. It is not tarnished in the air. Its sp. w. is 2.5.

Owing to its lightness, its great tenacity and strength, and the fact that it is not corroded in the air and not easily attacked by dilute acids, except hydrochloric acid, aluminum is a very useful metal, employed in the manufacture of articles in which lightness, strength and durability are especially desired.

Hydrochloric acid readily dissolves aluminum, forming the chloride,  $\text{AlCl}_3$ . Sulphuric acid attacks it very slowly. Nitric acid does not affect it except at the boiling point, and then only slowly. Hot solutions of the fixed alkalies dissolve the metal with formation of *aluminates*.

**761. Compounds.** Aluminum has but one oxide and does not form a carbonate. The structure of the compounds of Al is illustrated by the following examples:

$\text{Al}_2\text{O}_3$ , Aluminum oxide.

$\text{Al}(\text{OH})_3$ , Aluminum hydroxide, called "alumni hydras" in the Pharmacopœia.

$\text{AlCl}_3$ , Aluminum chloride (above  $360^\circ$ ;  $\text{Al}_2\text{Cl}_6$  at  $357^\circ$ ).

$\text{Al}_2(\text{SO}_4)_3$ , Aluminum sulphate.

$\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , Alum; alumen.

$\text{AlH}_4\text{N}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , Ammonia alum.

$\text{AlK}(\text{SO}_4)_2$ , Dried alum; alumen exsiccatum.

"Potash-alum," ammonia alum, and the sulphate, nitrate, acetate, chloride and bromide of aluminum are water-soluble and officinal, some of them being employed only in solution as disinfectants. The hydroxide and phosphate are insoluble.

The two common aluminum alums are manufactured on an extensive scale, being much used for industrial purposes. These alums are the materials used for the preparation of the hydroxide, which, in turn, is used for making the water-soluble aluminum salts by saturating the respective acids with it.

**762. Identification.** Aluminum compounds are colorless or white. The water-soluble salts have a decidedly astringent, sweetish-acid, but not metallic, taste. Their solutions, if the salts be of normal composition, have an acid reaction. They give a white precipitate of hydroxide with ammonia, whether ammonium chloride be present or not, whereby they may be distinguished from the salts of the alkali metals and the alkaline-earth metals, and from magnesium salts, which are not precipitated by ammonia in the presence of a sufficient amount of ammonium salt. Aluminum salts also give a white precipitate of hydroxide with KOH and NaOH, soluble in an excess of those reagents. Alkali carbonates also precipitate aluminum hydroxide from the solutions of aluminum salts.

When an aluminum salt is moistened with solution of cobaltous nitrate and then heated before the blow-pipe, the crust produced exhibits a blue color.

## CHAPTER LVII.

### CERIUM.

Symbol, Ce. At.w. 139.

**763.** Cerium occurs together with lanthanum, neodymium and praseodymium in the mineral *cerite* which is the chief material of which the cerium compounds are produced.

Cerium is a steel-gray metal of about 6.7 sp. w.

Among the compounds of this metal are:

$\text{Ce}_2\text{O}_3$ , Cerous oxide.

$\text{CeCl}_3$ , Cerous chloride.

$\text{Ce}(\text{OH})_3$ , Cerous hydroxide.

$\text{Ce}_2(\text{CO}_3)_3$ , Cerous carbonate.

$\text{Ce}_2(\text{C}_2\text{O}_4)_3$ , Cerous oxalate.

$\text{Ce}_2(\text{SO}_4)_3$ , Cerous sulphate.

$\text{Ce}(\text{NO}_3)_3$ , Cerous nitrate.

$\text{CeO}_2$ , Ceric oxide.

Although cerium by reason of its atomic weight falls into a tetrad group with titanium and zirconium, it seems to be, in several of its best known compounds, a triad and more closely related to aluminum than to any tetrad.

The cerous salts are stable. Ceric salts are reduced to cerous by boiling.

Cerium oxalate is officinal.

The carbonate and oxalate are insoluble; the sulphate, nitrate and chloride are soluble in water.

All these compounds are white or colorless.

## CHAPTER LVIII.

### ZINC.

Symbol, Zn, At.w. 65.3.

**764. Occurrence and production.** Zinc occurs in nature as *calamine*, which is composed of carbonate and silicate, as *zinc blende*, which is the sulphide, and as impure oxide, which is called red zinc ore.

The zinc ore is roasted to convert it into oxide, and this is reduced in a special furnace by heating it with charcoal.

**765. Description.** Zinc is a bluish-white metal of decided lustre, crystalline; brittle at ordinary temperatures, malleable between  $100^{\circ}$  and  $150^{\circ}$  C., but again brittle at  $200^{\circ}$ . Sp. w. 7.2: It melts at  $412^{\circ}$  C., and boils at about  $1000^{\circ}$  C.

The metal readily dissolves in dilute acids. Warm solutions of the alkalis also attack zinc. When zinc dissolves in an alkali solution the hydrogen of the alkali hydroxide gives up its place to the zinc so that a "zincate" of the alkali metal is formed. Yet zinc forms many stable salts in which it performs the basic function.

The molecule of zinc is monatomic in the state of vapor.

**766. Compounds.** The officinal zinc compounds and preparations include:

$\text{ZnO}$ , Zinc oxide; *zinci oxidum*. A white insoluble powder.

$\text{ZnCl}_2$ , Zinc chloride; *zinci chloridum*. A white, crystalline or granular, deliquescent, freely soluble salt.

$\text{ZnBr}_2$ , Zinc bromide; *zinci bromidum*. Freely soluble, crystalline, white.

$\text{ZnI}_2$ , Zinc iodide; *zinci iodidum*. Freely soluble, crystalline, white.

$\text{Zn}_3\text{P}_2$ , Zinc phosphide; *zinci phosphidum*. Gray, insoluble, porous solid.

$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (or, rather,  $\text{ZnH}_2\text{SO}_6 \cdot 6\text{H}_2\text{O}$ ), Zinc sulphate; *zinci sulphas*. "White vitriol." Crystalline, colorless, water-soluble.

$\text{Zn}_5(\text{OH})_2(\text{CO}_3)_2$ , Zinc carbonate; *zinci carbonas præcipitatus*. White insoluble powder.

$\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ , Zinc acetate; zinci acetas.

$\text{Zn}(\text{C}_8\text{H}_7\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ , Zinc valerate; zinci valerianas.

$\text{Zn}(\text{C}_{18}\text{H}_{33}\text{O}_2)_2$ , Zinc oleate; zinci oleas.

A solution of zinc chloride, liquor zinci chloridi, is also official, and an ointment of zinc oxide, besides a solution of zinc oleate in oleic acid.

The oxide, hydroxide, carbonate, oxalate, phosphide, phosphate and oleate of zinc are insoluble in water; the sulphate, nitrate, acetate, valerate, and halides are water-soluble.

**767. Properties.** Zinc compounds are white or colorless. The water-soluble salts have a disagreeable, bitter, astringent, metallic taste, and are poisonous.

The medicinal properties and uses of zinc compounds are various. Soluble zinc salts are astringents. The sulphate is also employed as an emetic. The oxide and carbonate and their ointments and cerates are employed externally as soothing applications and dressings.

**768. Preparation of zinc compounds.** The materials used for the production of zinc compounds are metallic zinc, zinc oxide and zinc carbonate for preparing water-soluble salts by solution in the requisite acids; zinc sulphate and zinc acetate are employed in the preparation of insoluble zinc compounds by precipitation.

The oxide is made either by the combustion of zinc in a sufficient supply of air at a high heat, or by the calcination of the carbonate.

**769. Reactions.** Zinc heated on charcoal before the blow-pipe volatilizes, leaving a coating of zinc oxide, which is yellow while hot, but becomes white on cooling. This coating, and all zinc salts, when moistened with cobaltous nitrate and heated strongly before the blow-pipe, assume a green color.

Solutions of zinc salts produce with KOH, NaOH, and  $\text{H}_4\text{NOH}$ , white precipitates which are soluble in an excess of the precipitant. They give white precipitates with the alkali carbonates and phosphates and with potassium ferrocyanide. With  $\text{H}_4\text{NSH}$  they afford a white precipitate of  $\text{ZnS}$  even in the presence of an excess of ammonia, wherein they differ from magnesium salts. No precipitate is formed by zinc salts on the addition of  $\text{H}_2\text{S}$  in the presence of free acid; but in alkaline solutions  $\text{ZnS}$  is thrown down by that reagent, and also in neutral solutions of the zinc salts of weak acids.

## CHAPTER LIX.

### CADMIUM.

Symbol, Cd. At. w. 112.

**770. Occurrence, production and description.** Cadmium is a companion of zinc, occurring in some zinc ores. It is obtained from zinc derived from cadmium-bearing zinc ores, and is separated from the zinc by distillation, the cadmium being the more volatile of the two metals.

**Description.** It is a soft, white metal, melting at about  $230^{\circ}$  C. and boiling at  $860^{\circ}$ . Its sp. w. is 8.6.

Cadmium resembles zinc very closely in its chemistry. Its molecule is monatomic; it is a dyad; dissolves readily in dilute acids.

**771. The compounds** of cadmium correspond to those of zinc, as shown by the following examples:

CdO, Cadmium oxide. A brown, insoluble powder.

Cd(OH)<sub>2</sub>, Cadmium hydroxide. White, insoluble powder.

CdS, Cadmium sulphide. A beautiful yellow insoluble powder.

CdCl<sub>2</sub>, Cadmium chloride. A volatile, colorless, crystalline salt.

CdI<sub>2</sub>, Cadmium iodide. Pearly, micaceous, water-soluble crystals.

CdBr<sub>2</sub>, Cadmium bromide. White, crystalline, water-soluble.

3CdSO<sub>4</sub>.8H<sub>2</sub>O, Cadmium sulphate. Colorless, water-soluble.

CdCO<sub>3</sub>, Cadmium carbonate. An insoluble white powder.

Cadmium sulphate and iodide are officinal. The iodide and bromide are employed in photography.

Cadmium compounds are poisonous.

**772. Identification.** The salts of cadmium are generally colorless. The sulphide is yellow, and acid solutions of cadmium salts give a yellow precipitate with H<sub>2</sub>S. The white precipitates produced by KOH and by ammonium carbonate are *not* soluble

in an excess of the precipitant. These reactions distinguish the cadmium salts from zinc salts.

If a piece of zinc be placed in the solution of a cadmium salt, the zinc becomes covered with small crystals of metallic cadmium.

When zinc containing cadmium is heated on charcoal before the blowpipe a ring of zinc oxide, pale yellow when hot and white when cold, is formed immediately surrounding the metal, while a brown ring of cadmium oxide is deposited further away around the zinc oxide ring.

## CHAPTER LX.

### MAGNESIUM.

Symbol, Mg. At. w., 24.2.

**773. Occurrence and production.** Magnesium occurs principally in the forms of carbonate and silicate in certain rock formations. *Magnesite* is magnesium carbonate, and *dolomite* is composed of magnesium carbonate and calcium carbonate. "French chalk" or "talcum" is magnesium silicate; "meerschauum" and "asbestos" also consist of magnesium silicate.

The sulphate and chloride occur in the waters of some mineral springs and in sea water.

The metal is produced by the reduction of the chloride by fusion with metallic sodium, fluorspar being added to serve as a flux.

**774. Description.** Magnesium is a white metal capable of high polish. It oxidizes slowly in moist air. Can be made into wire by forcing the metal, softened by heat, through apertures of the requisite diameter, and the wire can be converted into ribbons by being pressed between rollers. When ignited magnesium burns with a light of dazzling brilliancy to oxide.

The "flash-light" employed in photography is produced by burning magnesium. The sp. w. of magnesium is only 1.74. It melts at 700°, and volatilizes at a sufficiently high temperature.

It does not decompose water at the ordinary temperatures, but at the boiling point water gives up its oxygen to magnesium, hydrogen being liberated.

**775. Compounds.** The compounds of magnesium resemble in many respects those of zinc and cadmium. The three metals named constitute the "zinc group;" but, although they form a triad, the middle member of which has an atomic weight equal to about one-half of the sum of the atomic weights of the other two, magnesium is the most powerful positive element in this triad, whereas the alkali metals and the alkaline-earth metals follow the general rule that the element having the greatest atomic weight forms the most powerful base.

Zinc and cadmium fall into the same group with mercury in the periodic system, but magnesium stands between sodium and aluminum, beryllium and calcium, close to the alkaline-earth metals and the alkali metals.

The oxides, hydroxides, carbonates, phosphates and oxalates of magnesium, zinc and cadmium are insoluble in water, but their sulphates are soluble. In these respects they differ from the metals of the alkaline earths. The carbonates of the metals of the zinc group, as obtained by precipitation from the solutions of their normal salts, are basic, while the precipitated carbonates of the alkaline earth metals are normal; but magnesium carbonate is soluble in a solution of carbonic acid, resembling in that respect the carbonate of calcium, while zinc carbonate is not soluble in carbonic acid solution.

Magnesium sulphide is water-soluble, but not the sulphides of Zn and Cd. Zinc is capable of assuming acidic functions, forming zincates; but magnesium is not.

**776.** The **official magnesium compounds** include:

MgO, Magnesium oxide; magnesii oxidum. Called "magnesia" in the American Pharmacopœia. A white, insoluble powder. Two varieties exist: a "light magnesia" and a "heavy magnesia."

MgCl<sub>2</sub>, Magnesium chloride; magnesii chloridum. Colorless, crystalline. Water-soluble.

MgBr<sub>2</sub>, Magnesium bromide; magnesii bromidum. Colorless, crystalline. Soluble.

MgH<sub>2</sub>SO<sub>6</sub>·6H<sub>2</sub>O (commonly written MgSO<sub>4</sub>·7H<sub>2</sub>O), Magnesium sulphate; magnesii sulphas. Called "Epsom salt." Colorless, crystalline. Readily soluble.

MgSO<sub>3</sub>, Magnesium sulphite; magnesii sulphis.

Mg<sub>3</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O, Common magnesium carbonate; magnesii carbonas of the pharmacopœias. An insoluble white powder, occurring in two forms—"light" and "heavy."

Magnesium citrate, a white powder practically insoluble in water, but soluble in a solution of citric acid, is also official.

The oxide and carbonate are "antacids." The water-soluble salts are saline cathartics. Magnesium hydroxide produced by

mixing "light magnesia" with water, is used as an antidote for arsenic.

**777. General properties.** The magnesium compounds generally are colorless or white. The water-soluble magnesium salts formed by the stronger acids, as the sulphate, chloride, etc., have a bitter saline taste; but the citrate solution (made with the aid of free citric acid) is *not* bitter; and the tartrate and acetate are also comparatively free from bitterness.

The *materials* employed for the production of magnesium compounds for medicinal uses are: Magnesium carbonate for the preparation of the oxide by calcination; carbonate as well as oxide for the preparation of the water-soluble salts (except the sulphate which is manufactured on a large scale and is more abundant and cheaper than any other magnesium compound); and the sulphate is used for the production of some insoluble magnesium compounds, as the carbonate, by precipitation.

**778. Reactions.** Solutions of magnesium salts afford white precipitates of hydroxide with KOH and NaOH, and of basic carbonate with the alkali carbonates. These precipitates are not soluble in an excess of the respective reagents named. Ammonia does not cause complete precipitation of the magnesium as hydroxide, but forms a soluble double-salt with a portion of the magnesium compound, and this double-salt is not decomposed by more ammonia. Hence, if ammonium chloride be added in sufficient quantity to the solution of a magnesium salt, the subsequent addition of ammonia produces no precipitation. Such an ammoniacal solution is not precipitated by oxalic acid, whereby magnesium salts may be distinguished from calcium salts, nor does it produce a precipitate with ammonium carbonate. But a solution of sodium phosphate produces in ammoniacal solutions of magnesium salts a white crystalline precipitate of magnesium-ammonium phosphate; this precipitate, however, does not appear until after some time if the solution is very dilute.

Solutions of magnesium salts are not precipitated by dilute sulphuric acid, whereby they may be distinguished from the salts of barium and strontium. They may be distinguished from salts of zinc and cadmium by  $H_2S$ , which causes no precipitate in solutions of magnesium salts, but a white precipitate with zinc and a yellow one with cadmium.

## CHAPTER LXI.

### CALCIUM.

Symbol, Ca. At. w., 40.

**779. Occurrence and production.** Calcium occurs abundantly in the form of limestone, chalk and marble, all of which consist of more or less impure calcium carbonate; and the silicate and other calcium compounds are contained in various kinds of igneous rocks.

The metal is obtained from its chloride by electrolysis.

**780. Description.** It is a soft yellowish metal, which may be kept in dry air without oxidation but oxidizes in moist air. When put in water it immediately decomposes the water, forming calcium hydroxide and liberating hydrogen. It may be ignited, and burns with a yellow flame. Its sp. w. is 1.6.

Metallic calcium is of no industrial value.

**781. Industrial uses** of common lime compounds: *Hydraulic cement*, such as "Portland cement," etc., is made by calcining limestone containing clay and silica; on being mixed with water this cement becomes extremely hard through the formation of calcium silicate and calcium carbonate.

Building *mortar*, made of "quick lime," sand and water, hardens on drying in a way similar to the hardening of cement.

Dried *gypsum* or nearly anhydrous calcium sulphate, in powder, when mixed with water, forms crystallized calcium sulphate, which constitutes the "*plaster of paris*," of which wall plastering, statuary, and surgical plaster casts and dressings are made.

*Quick lime*, or building lime, is calcium oxide, made by calcining limestone in lime kilns. *Slaked lime* is calcium hydroxide formed by adding water to the oxide.

**782. Compounds.** The structure of calcium compounds is illustrated by the following examples of officinal substances:

CaO, Calcium oxide; calcii oxidum. Called calx, *lime*, in the American Pharmacopœia. A white solid forming hydroxide with water.

- $\text{Ca}(\text{OH})_2$ , Calcium hydroxide; *calcii hydroxidum*. Called "calcium hydrate" in the pharmacopœias. A white powder, very sparingly soluble in water, the solution being commonly called "lime water," and, in the American Pharmacopœia, *liquor calcis*.
- $\text{CaCl}_2$ , Calcium chloride; *calcii chloridum*. A white deliquescent hard solid.
- $\text{CaBr}_2$ , Calcium bromide; *calcii bromidum*. A white, granular, deliquescent salt.
- $\text{CaI}_2$ , Calcium iodide; *calcii iodidum*. A white, deliquescent salt.
- $\text{Ca}(\text{NO}_3)_2$ , Calcium nitrate; *calcii nitras*. Colorless, water-soluble.
- $\text{CaCO}_3$ , Calcium carbonate; *calcii carbonas*. White, amorphous, insoluble powder. The Pharmacopœia contains precipitated calcium carbonate as well as prepared chalk.
- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , Calcium sulphate, or "gypsum."
- $\text{CaSO}_4$ , Dried calcium sulphate; *calcii sulphas exsiccatus*. A white powder, used for preparing "plaster of paris."
- $\text{CaSO}_3$ , Calcium sulphite; *calcii sulphis*. White, granular. Soluble.
- $\text{Ca}_3(\text{PO}_4)_2$ , Calcium phosphate; *calcii phosphas*. An amorphous, insoluble white powder. The precipitated calcium phosphate of the American Pharmacopœia is of this composition. This compound is often referred to as the "bone phosphate of calcium," being the chief constituent of bone.
- $\text{CaHPO}_4$ , Calcium hydrogen phosphate. This is the "calcium phosphate" of several pharmacopœias. A white, crystalline, insoluble powder.
- $\text{CaH}_4(\text{PO}_4)_2$ , Acid calcium phosphate. White or colorless. Water soluble.
- $\text{Ca}(\text{PH}_2\text{O}_2)_2$ , Calcium hypophosphite; *calcii hypophosphis*. White or colorless, crystalline. Readily water-soluble.
- $\text{Ca}(\text{ClO})_2$ , Calcium hypochlorite; *calcii hypochloris*. A soluble colorless salt contained together with calcium chloride in the "chlorinated lime," *calx chlorinata*, of the Pharmacopœia. "Chlorinated lime" is com-

monly called "chloride of lime" or "bleaching powder."

$\text{CaS}$ , Calcium sulphide; *calcii sulphidum*. A yellow, water-soluble, hygroscopic compound contained together with calcium sulphate and other substances in the "sulphurated lime," *calx sulphurata*, of the *Pharmacopœia*.

$\text{CaSS}_4$ , Calcium tetra-thiosulphate, commonly called calcium pentasulphide,  $\text{CaS}_5$ , contained together with other compounds in the yellowish-red solution obtained by boiling sulphur and calcium hydroxide together in water.

$\text{Ca}(\text{C}_3\text{H}_5\text{O}_3)_2$ , Calcium lactate; *calcii lactas*. White. Water-soluble.

**783. General description.** Calcium compounds are white or colorless. Those that are soluble possess, generally, a disagreeable, caustic, acrid, or bitterish taste.

The hydroxide and sulphate are quite sparingly *water-soluble*. Normal carbonate, phosphate and oxalate are *insoluble*. The carbonate is soluble in a carbonic acid solution. Acid phosphate is water-soluble. Halides, sulphide, nitrates and acetate are *freely soluble*.

**784. Preparation.** Soluble calcium compounds are prepared from the carbonate or the hydroxide. The insoluble ones are generally made from the chloride by precipitation. Oxide is made by calcining the carbonate; the hydroxide by adding water to the oxide.

**785. Reactions.** Solutions of calcium salts are not precipitated by ammonia. They form a white precipitate with the alkali carbonates. Strong solutions of calcium salts form a white crystalline precipitate with sulphates or sulphuric acid; but dilute solutions are not precipitated by any sulphate. With oxalic acid and other oxalates even dilute solutions of calcium compounds form a white precipitate; the precipitated calcium oxalate is somewhat soluble in nitric acid, but insoluble in acetic acid. When a solution of a calcium salt has been precipitated with sulphuric acid or any other sulphate, it will still produce a white precipitate with oxalic acid, and the calcium salts are thereby distinguished from the salts of barium and strontium, which are completely precipitated by sulphates.

## CHAPTER LXII.

### STRONTIUM AND BARIUM.

**786. Strontium**, Sr. at. w. 87.5, occurs rather sparingly and in the form of sulphate and carbonate. The sulphate is called *celestine*, and the carbonate *strontianite*.

The metal is obtained by the electrolysis of the chloride. It strongly resembles calcium, but is much heavier, having the sp. w. 2.5.

**787.** The compounds of strontium are closely analogous to those of calcium and barium in structure, solubilities and other properties.

Among the common strontium compounds are:

SrO, Strontium oxide. White. Forms hydroxide with water.

SrCl<sub>2</sub>.6H<sub>2</sub>O, Strontium chloride. Colorless, crystalline, deliquescent.

SrBr<sub>2</sub>.6H<sub>2</sub>O, Strontium bromide; strontii bromidum. Colorless, crystalline, deliquescent.

SrI<sub>2</sub>.6H<sub>2</sub>O, Strontium iodide; strontii iodidum. Colorless, crystalline, deliquescent.

Sr(C<sub>3</sub>H<sub>5</sub>O<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O, Strontium lactate; strontii lactas. White, crystalline or granular. Readily soluble.

SrCO<sub>3</sub>, Strontium carbonate. Insoluble white powder.

SrSO<sub>4</sub>, Strontium sulphate. Insoluble white powder.

Sr(NO<sub>3</sub>)<sub>2</sub>, Strontium nitrate. Colorless, crystalline. Readily soluble.

The strontium compounds are white or colorless. Their reactions have been mentioned in connection with the description of the alkaline-earth metals. Strontium imparts a beautiful red color to flame.

**788. Barium**, Ba. at. w. 137, occurs in the form of sulphate as "heavy spar" in caves on Put-in-Bay Island, near the Ohio lake shore, and in other places. Also as carbonate.

The metal resembles calcium and strontium, but barium has the sp. w. 4.

The compounds resemble those of calcium and strontium and include:

$\text{BaO}$ , Barium oxide, or "baryta." A white compact solid forming hydroxide with water.

$\text{BaO}_2$ , Barium dioxide; barii dioxidum. Also called "barium peroxide." A grayish-white powder, forming hydrogen dioxide and barium hydroxide with water, in the presence of acids.

$\text{Ba}(\text{NO}_3)_2$ , Barium nitrate. A colorless, crystalline, water-soluble salt.

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , Barium chloride. Colorless, crystalline. Soluble.

$\text{Ba}(\text{OH})_2$ , Barium hydroxide. White, amorphous or crystalline (with water). Soluble in 20 parts of water.

$\text{BaSO}_4$ , Barium sulphate. Occurs in nature in large colorless crystals. Insoluble. Sp. w., 4.59.

$\text{BaCO}_3$ , Barium carbonate. Insoluble white powder.

$\text{BaS}$ , Barium sulphide. Water-soluble.

The chloride and the nitrate are employed as reagents for the detection and determination of sulphuric acid.

No barium compound is employed for medicinal purposes.

The carbonate is used as a rat-poison.

The reactions of barium compounds have been referred to in paragraph 459 and paragraph 660. They impart a green color to flame.

## CHAPTER LXIII.

### LITHIUM.

Symbol, Li. At. w., 7.

**789. Occurrence and production.** Lithium occurs in very small quantities in the waters of some mineral springs, and in the ashes of some plants among which tobacco is one. *Lepidolite* and other minerals contain lithium silicate associated with other compounds, and the lepidolite of Australia is the chief source of lithium.

The metal is obtained from its chloride by electrolysis. It is soft, silver-white, and has the sp. w. 0.589. It decomposes water, and burns in the air with an intensely red flame.

**790. The official lithium compounds include:**

LiCl, Lithium chloride; lithii chloridum. Colorless or white, crystalline or granular. Soluble.

LiBr, Lithium bromide; lithii bromidum. White, granular. Freely soluble.

Li<sub>2</sub>CO<sub>3</sub>, Lithium carbonate; lithii carbonas. A white, amorphous powder. Comparatively sparingly soluble in water.

Li<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·4H<sub>2</sub>O, Lithium citrate; lithii citras. White powder. Freely soluble.

LiC<sub>7</sub>H<sub>5</sub>O<sub>2</sub>, Lithium benzoate; lithii benzoas. White, granular or crystalline. Soluble.

LiC<sub>7</sub>H<sub>5</sub>O<sub>3</sub>, Lithium salicylate; lithii salicylas. A freely soluble white powder.

Lithium carbonate is employed as an "antacid" and "anti-lithic." The bromide is useful in preference to the corresponding salt of potassium or sodium chiefly on account of the low atomic weight of the metal, as a result of which the lithium bromide contains over 91 per cent of bromine, whereas the potassium bromide contains only 66 per cent, and the sodium bromide only about 77 per cent of bromine.

**791. Properties and reactions.** Lithium compounds are white or colorless. The phosphate is nearly insoluble, and the hydroxide and carbonate sparingly soluble. The chloride, salicylate, and citrate are deliquescent; but the hydroxide and the carbonate are not so.

Lithium salts mixed with alcohol color the flame of the blow-pipe, or of a Bunsen burner, or spirit lamp, beautifully crimson. The red line of the spectrum given by Li is extremely characteristic and sensitive.

## CHAPTER LXIV.

### SODIUM.

Symbol, Na. At. w., 23.

**792. Occurrence and production.** Sodium occurs abundantly in the form of common salt, sodium chloride, in salt beds and springs and in sea water. It also occurs as nitrate in the salt-petre beds of Chili; also as sulphate and carbonate.

The metal is produced by heating and distilling a mixture of sodium carbonate, charcoal and either chalk or iron carbide in steel retorts. It is also obtained by electrolysis from its chloride or its hydroxide.

**793. Description.** It is a soft silver-white metal which must be kept in a liquid hydrocarbon, such as naphtha or benzin, to prevent oxidation. Its sp. w. is 0.97. It reacts vigorously with water, forming sodium hydroxide and liberating hydrogen.

**794.** The carbonate or "**sal sodae**" is manufactured on an immense scale from the chloride. The chloride is first treated with sulphuric acid, the products being sodium sulphate and hydrochloric acid; the sodium sulphate is strongly heated with coal or charcoal and chalk, which results in the reduction of the sodium sulphate to sodium sulphide and this reacts with the calcium carbonate, forming calcium sulphide and sodium carbonate. The crude sodium carbonate, called "soda ash," is purified by several crystallizations. This is *Le Blanc's process*.

Another and now more commonly practiced process is that of *Solvay*. It consists in treating the sodium chloride with ammonia and carbon dioxide, whereby sodium bicarbonate and ammonium chloride are formed; the sodium bicarbonate, being very sparingly soluble in the solution of ammonium chloride, separates and is turned into normal carbonate by heat, after which the dry carbonate is dissolved in water and purified by repeated crystallizations.

The *cryolite process* is also largely employed. The mineral called cryolite is a double fluoride of aluminum and sodium. This is heated with lime ( $\text{CaO}$ ), which results in the formation of cal-

cium fluoride and sodium aluminate, a compound of the formula  $(\text{Na}_2\text{O})_3\text{Al}_2\text{O}_3$ , which is water-soluble and, therefore, readily separated from the insoluble calcium fluoride. When carbon dioxide is passed into the solution of the sodium aluminate, aluminum hydroxide precipitates and sodium carbonate is formed in the liquid and is crystallized out.

**795.** The official sodium compounds include:

$\text{NaOH}$ , Sodium hydroxide; sodii hydroxidum. This is called "soda" in the American Pharmacopœia. It is also commonly called "sodium hydrate," and "caustic soda." It is a compact white solid, freely soluble in water. A 5 per cent solution of it is the "liquor sodæ."

$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , Sodium carbonate; sodii carbonas. Colorless crystals. Readily soluble in water.

$\text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ , Dried sodium carbonate; sodii carbonas exsiccatus. White amorphous powder. Readily soluble.

$\text{Na}_2\text{CO}_3$ , Anhydrous sodium carbonate. White powder. Soluble.

•  $\text{NaHCO}_3$ , Sodium bicarbonate; sodii bicarbonas. Acid carbonate of sodium. White powder. Not freely soluble.

$\text{NaCl}$ , Sodium chloride; sodii chloridum. Colorless crystals or a white granular salt. Readily soluble.

$\text{NaBr}$ , Sodium bromide; sodii bromidum. Colorless or white crystals or granular powder. Freely soluble.

$\text{NaI}$ , Sodium iodide; sodii iodidum. Colorless crystals or a white granular powder (unless partially decomposed). Very freely soluble.

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , Sodium sulphate; sodii sulphas. Glauber's salt. Colorless crystals. Freely soluble. Efflorescent.

$\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ , Sodium sulphite; sodii sulphis. Colorless crystals. Readily soluble. Efflorescent.

$\text{NaHSO}_3$ , Sodium bisulphite; sodii bisulphis. A white granular crystalline salt. Readily water-soluble.

$\text{Na}_2\text{SO}_3 \cdot \text{S} \cdot 5\text{H}_2\text{O}$  (usually written  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ), Sodium thiosulphate. Commonly called sodium hyposul-

phite; sodii hyposulphis. Colorless crystals. Readily soluble.

$\text{Na}_2\text{SO}_3$ , Sodium hyposulphite.

$\text{NaNO}_3$ , Sodium nitrate; sodii nitras. Colorless crystals. Readily soluble.

$\text{NaNO}_2$ , Sodium nitrite; sodii nitris. Colorless crystals, or a white, fused salt. Freely soluble.

$\text{NaClO}_3$ , Sodium chlorate; sodii chloras. Colorless crystals. Readily soluble.

$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , Sodium phosphate; sodii phosphas. Colorless crystals. Efflorescent. Freely soluble.

$\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ , Sodium pyrophosphate; sodii pyrophosphas. Colorless crystals. Soluble.

$\text{NaPH}_2\text{O}_2$ , Sodium hypophosphite; sodii hypophosphis. Colorless crystals or white granular powder. Deliquescent. Freely soluble.

$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , Sodium tetraborate. Called sodium borate, sodii boras, in the Pharmacopœia. Commonly called "borax." Also called sodium pyroborate. Colorless crystals. Slightly efflorescent. Soluble.

$\text{Na}_2\text{HASO}_4 \cdot 7\text{H}_2\text{O}$ , Sodium arsenate; sodii arsenas. Colorless crystals. Readily soluble.

$\text{NaOCl}$ , Sodium hypochlorite. A colorless salt contained in the officinal "solution of chlorinated soda" or "Labarraque's solution."

$\text{NaSO}_3\text{C}_6\text{H}_4\text{OH} \cdot 2\text{H}_2\text{O}$ , Sodium phenolsulphonate. Called in the Pharmacopœia "sodium sulphocarbolate;" sodii sulphocarbolas. The paraphenolsulphonate of sodium. Colorless crystals. Somewhat efflorescent. Readily soluble.

$\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ , Sodium acetate; sodii acetas. Colorless crystals, or a granular crystalline powder. Somewhat efflorescent. Freely soluble.

$\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ , Sodium tartrate; sodii tartras. White, granular. Very soluble.

$\text{NaHC}_4\text{H}_4\text{O}_6$ , Sodium bitartrate; sodii bitartras. White powder. Sparingly soluble.

$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ , Sodio-potassium tartrate; potassii et sodii tartras. Rochelle salt. Colorless crystals, or a white powder. Very freely soluble.

$2\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 11\text{H}_2\text{O}$ , Sodium citrate; sodii citras. Colorless crystals, or white powder. Freely soluble.

$\text{NaC}_5\text{H}_9\text{O}_2$ , Sodium valerate or valerianate; sodii valerianas. Colorless crystals. Readily soluble.

$\text{NaC}_7\text{H}_5\text{O}_3$ , Sodium salicylate; sodii salicylas. White powder. Freely soluble.

$\text{NaC}_7\text{H}_5\text{O}_2$ , Sodium benzoate; sodii benzoas. White, amorphous powder. Freely soluble.

$\text{NaC}_{18}\text{H}_{33}\text{O}_2$ , Sodium oleate. The chief constituent of hard soap.

"Sodium ethylate," "sodium ethyl sulphate," "sodium santoninate," and other sodium compounds are occasionally used.

**796. Uses.** The sodium compounds are employed pharmaceutically and medicinally for various widely different purposes. The carbonate is used principally as the "raw material" out of which other sodium preparations are produced and also in the preparation of other carbonates. The phosphate of sodium is mainly employed for the production of other phosphates and of pyrophosphates. The hydroxide is employed in the preparation of precipitated metallic oxides. The bicarbonate is employed medicinally as an antacid. Other sodium compounds, as the sulphate and Rochelle salt, are saline cathartics. But most of the sodium compounds owe their medicinal value to the negative radical in them; thus the benzoate is used not because it is a sodium salt, but because it is a benzoate, and thus it is with the salicylate, the bromide, the valerate, etc.

**797. General properties.** The sodium compounds are white or colorless. They are all water-soluble except sodium antimonate; but the acid sodium tartrate, or bitartrate of sodium is not freely soluble.

Sodium salts contain water of crystallization more frequently than the potassium salts, and many of the hydrous crystallized salts of sodium are efflorescent, while others may dissolve in their water of crystallization at a temperature somewhat above the ordinary room temperature (as, for instance, sodium phosphate). But the hydroxide, iodide, nitrate and hypophosphite are deliquescent in moist air. The hydroxide, after absorbing moisture upon the surface, takes up carbon dioxide and becomes converted into dry carbonate.

Sodium hydroxide, carbonate, bicarbonate, acetate, phosphate, pyrophosphate, arsenate, nitrite, and tetraborate have an alkaline reaction on test paper. Bisulphite and salicylate have an acid reaction (the salicylate because it must necessarily contain a slight excess of salicylic acid). The chloride, bromide, iodide, sulphate, thiosulphate, nitrate, chlorate, hypophosphite, tartrate and citrate have a neutral reaction.

**798. Reactions.** Solutions of sodium salts give a white crystalline precipitate with potassium antimonate, and are not precipitated by platinum chloride. They are not precipitated by an excess of tartaric acid unless the solutions are strong.

Sodium compounds impart a yellow color to flame, and give a very characteristic spectrum with a yellow band.

## CHAPTER LXV.

### POTASSIUM.

Symbol, K. At. w., 39.

**799. Occurrence.** Potassium occurs abundantly in the granite rocks in the form of silicate in combination with other silicates. Hence it also occurs in soils derived from these rocks, and in plants growing in such soils. Plant ashes accordingly contain potassium carbonate; hence the name "pot-ash" was given to the crude potassium carbonate leached out from wood ashes, and the name potassium to the metal itself.

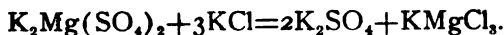
Acid tartrate of potassium, called "tartar" and "argols," is deposited from the fermented juice of grapes in the making of wine, and the purified potassium bitartrate from this source is called "cream of tartar" and, in the old latinic terminology, "cremor tartari" and "tartarus depuratus."

But the most abundant source of potassium is now the potassium salts found associated with magnesium salts in the immense salt beds at Stassfurth, Germany. The salts contained in the Stassfurth salt mines include *kieserite*, which is magnesium sulphate with one molecule of water,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ; *sylvine*, which is potassium chloride,  $\text{KCl}$ ; *kainite*, a double sulphate of potassium and magnesium,  $\text{K}_2\text{Mg}(\text{SO}_4)_2$ ; and *carnallite*, a double chloride of potassium and magnesium,  $\text{KMgCl}_2$ .

The magnesium sulphate and potassium chloride together, in solution, form the double sulphate and double chloride:



The double sulphate, when boiled with more potassium chloride yields potassium sulphate and double chloride of potassium and magnesium:



The double chloride,  $\text{KMgCl}_2$ , splits slowly in water into  $\text{KCl}$  and  $\text{MgCl}_2$ , so that the potassium chloride can be crystallized out

and thus separated from the more freely soluble magnesium chloride.

The KCl is used over again with fresh portions of the double sulphate to make more potassium sulphate, which is readily separated by crystallization.

The potassium sulphate thus obtained is then employed for the manufacture of potassium carbonate by a process similar to Le Blanc's method for the production of sodium carbonate from sodium sulphate. The potassium carbonate obtained is purified and then constitutes the material out of which most of the other potassium salts are prepared.

For pharmaceutical potassium compounds the Pharmacopœias generally employ potassium bicarbonate instead of normal potassium carbonate. This is because the bicarbonate can be crystallized and is not deliquescent, whereas the carbonate is amorphous and eagerly absorbs moisture. Hence the normal carbonate is liable to be more variable than the bicarbonate. The latter is easily prepared by exposing the carbonate to the action of carbon dioxide and then crystallizing the bicarbonate from the solution.

**800. Description.** Potassium is a silver-white, soft metal, lustrous when freshly cut, but tarnishing very rapidly in the air. It is necessarily kept submerged in benzine or some other liquid hydrocarbon to prevent oxidation.

The sp. w. of this metal is 0.86. When placed upon water it causes its decomposition, combining with hydroxyl to form potassium hydroxide, which dissolves in the rest of the water present, and hydrogen is liberated. The hydrogen is ignited by the heat of the reaction so that flame appears.

**801.** The official potassium compounds include:

KOH, Potassium hydroxide; potassii hydroxidum. Called "potassa" in the American Pharmacopœia. Also called "caustic potash," and "potassium hydrate." A deliquescent white solid. A 5 per cent solution called "liquor potassæ" is also official. A mixture of equal parts of KOH and CaO is official under the title of "potassa cum calce."

K<sub>2</sub>CO<sub>3</sub>, Potassium carbonate; potassii carbonas. "Pearl ash" and "potash" are names commonly given to crude or

impure potassium carbonate derived from wood ashes. Commercial potassium carbonate pure enough for medicinal and pharmaceutical uses contains moisture; it is usually approximately  $2K_2CO_3 \cdot 3H_2O$ . White, deliquescent.

$KHCO_3$ , Potassium bicarbonate; potassii bicarbonas. Colorless crystals. Soluble in water.

$KCl$ , Potassium chloride; potassii chloridum. Colorless crystals or a white granular salt. Readily soluble.

$KBr$ , Potassium bromide; potassii bromidum. Colorless or white crystals, or a granular powder. Readily soluble.

$KI$ , Potassium iodide; potassii iodidum. Colorless or translucent whitish crystals, or a granular powder. Very freely soluble.

$KCN$ , Potassium cyanide; potassii cyanidum. Called "prussiate of potash." White pieces, amorphous. Deliquescent. Extremely poisonous.

$K_3Fe(CN)_6$ , Potassium ferricyanide; potassii ferricyanidum. Dark red crystals. Readily soluble.

$K_4Fe(CN)_6 \cdot 3H_2O$ , Potassium ferrocyanide; potassii ferrocyanidum. Called also "yellow prussiate of potash." Pale yellow, transparent or translucent crystals. Readily soluble.

$K_2SO_4$ , Potassium sulphate; potassii sulphas. Hard, colorless, transparent crystals. Soluble.

$K_2SO_3$ , Potassium sulphite; potassii sulphis. White powder. Soluble.

$KNO_3$ , Potassium nitrate; potassii nitras. Colorless crystals, or a white crystalline granular salt. Readily soluble.

$KClO_3$ , Potassium chlorate; potassii chloras. Colorless crystals. Soluble.

$K_2HPO_4$ , Potassium phosphate; potassii phosphas. White, granular. Deliquescent.

$KPH_2O_2$ , Potassium hypophosphite; potassii hypophosphis. A white crystalline powder. Very deliquescent.

$K_2HASO_3$ , Potassium arsenite. Contained in "liquor potassii arsenitis," or Fowler's solution.

- $K_2SS_2$  (generally written  $K_2S_3$ ), potassium hypo-thiosulphite. Commonly called "potassium trisulphide." Brown, amorphous. Deliquescent. Contained in "sulphurated potassa" or "liver of sulphur."
- $K_2Cr_2O_7$ , Potassium dichromate; potassii dichromas. Called "potassii bichromas" in the Pharmacopœias. Orange-red, transparent crystals. Soluble.
- $KMnO_4$ , Potassium permanganate; potassii permanganas. Long, slender, dark purple crystals. Soluble.
- $KC_2H_3O_2$ , Potassium acetate; potassii acetas. White crystalline or granular. Deliquescent.
- $K_2C_4H_4O_6 \cdot H_2O$ , Potassium tartrate; potassii tartras. White or colorless, crystalline. Readily soluble.
- $KNaC_4H_4O_6 \cdot 4H_2O$ , Potassium-sodium tartrate; potassii et sodii tartras. "Rochelle salt." Colorless crystals or white powder. Very freely soluble.
- $KHC_4H_4O_6$ , Potassium bitartrate; potassii bitartras. "Cream of tartar." Colorless crystals, or a white powder. Sparingly soluble.
- $K_3C_6H_5O_7 \cdot H_2O$ , Potassium citrate; potassii citras. White granular salt. Readily soluble.
- $2KC_7H_5O_3 \cdot H_2O$ , Potassium salicylate; potassii salicylas. White powder. Freely soluble.
- $KC_7H_5O_2 \cdot 3H_2O$ , Potassium benzoate; potassii benzoas. White granular powder. Freely soluble.

**802. Medicinal uses.** The potassium salts, in common with the salts of sodium and ammonium, differ radically from the compounds of the heavy metals in that the latter owe their medicinal properties in all cases to the metallic elements, whereas the salts of the alkali metals and ammonium are frequently employed on account of their negative salt radicals.

Potassium carbonate and bicarbonate are used as "antacids," and some of the potassium salts are used as saline laxatives, or in "fever mixtures." But the bromide is used for its bromine, the iodide for its iodine, the salicylate for its salicylate radical, etc.

The hydroxide, carbonate, bicarbonate, iodide, and some other potassium salts are frequently employed as materials for the production of other compounds.

**803. Properties and reactions.** Potassium compounds are white or colorless, with the exception of ferricyanide, which is dark red, ferrocyanide, which is light yellow, sulphurated potassa, which is liver-brown or greenish-yellowish brown, the dichromate, which is orange-red, and permanganate, which is dark purple.

They are all water-soluble; but potassium-platinum chloride is almost insoluble and the bitartrate sparingly soluble.

The hydroxide, carbonate, acetate, citrate, cyanide, hypophosphite, and borax tartar are deliquescent.

The hydroxide, carbonate, bicarbonate, acetate, cyanide, and sulphurated potassa are alkaline to litmus paper; bichromate and bitartrate have an acid reaction.

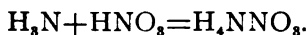
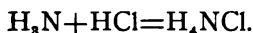
Potassium imparts a violet color to flame and produces a spectrum characterized by one red and one violet band.

## CHAPTER LXVI.

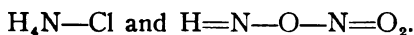
### AMMONIUM COMPOUNDS.

**804.** The salts formed by ammonia,  $\text{H}_3\text{N}$ , with the acids are regarded as containing the radical  $\text{H}_4\text{N}$ , called *ammonium*, and the salts of ammonium resemble those of potassium and sodium so closely and are so common that no work on inorganic chemistry is complete which does not include the ammonium compounds analogous to the inorganic compounds of potassium and sodium.

When ammonia reacts with an acid the reaction results in but one product and hence appears to be a simple synthesis or addition, as shown in the following equations.



But it will be seen that in both cases the hydrogen of the acid is separated from the negative radical with which it was united in the acid molecule, the relative position of the elements being necessarily, by reason of the valence of nitrogen, as follows:



**805.** The present chief **source** of ammonia is the "ammoniacal liquor," which is obtained as a bye-product in the manufacture of illuminating gas by the dry distillation of coal. The alkaline ammoniacal liquor is first heated with slaked lime (calcium hydroxide in the form of "milk of lime"), the gas,  $\text{H}_3\text{N}$ , is passed through charcoal to purify it, and then into receivers containing water which is saturated.

The ammonia water thus produced is neutralized with sulphuric acid, the sulphate purified and recovered from the solution, and then decomposed with lime again, whereby a cleaner  $\text{H}_3\text{N}$  is obtained. Or chloride of ammonium is made from the ammonia with hydrochloric acid, the ammonium chloride purified by sublimation, and a purer ammonia produced from the purified ammonium chloride.

**806.** The **official ammonium compounds** are many. They include:

$\text{H}_4\text{NOH}$ , Ammonium hydroxide; ammonii hydroxidum. Exists only in solution. The Pharmacopœia contains one water-solution representing 10 per cent of  $\text{H}_3\text{N}$ , or nearly 20.6 per cent of  $\text{H}_4\text{NOH}$ , and another representing 28 per cent of  $\text{H}_3\text{N}$ , or nearly 57.65 per cent of  $\text{H}_4\text{NOH}$ ; also an alcoholic solution representing 10 per cent of  $\text{H}_3\text{N}$ .

$\text{H}_4\text{NHCO}_3 \cdot \text{H}_4\text{NH}_2\text{NCO}_2$ , Official ammonium carbonate; ammonii carbonas. Colorless, transparent or translucent hard pieces; soluble.

$(\text{H}_4\text{N})_2\text{CO}_3$ , Normal ammonium carbonate. Colorless, crystalline; soluble.

$\text{H}_4\text{NHCO}_3$ , ammonium bicarbonate. Colorless, crystalline; soluble.

$\text{H}_4\text{NCl}$ , Ammonium chloride; ammonii chloridum. Colorless crystalline, or a white, granular, crystalline powder; soluble.

$\text{H}_4\text{NBr}$ , Ammonium bromide; ammonii bromidum. Colorless or white, crystalline; soluble.

$\text{H}_4\text{NI}$ , ammonium iodide; ammonii iodidum. Colorless or white, crystalline. Very freely soluble.

$(\text{H}_4\text{N})_2\text{SO}_4$ , ammonium sulphate; ammonii sulphas. Colorless crystals; freely soluble.

$\text{H}_4\text{NNO}_3$ , Ammonium nitrate; ammonii nitras. Colorless crystals; freely soluble.

$\text{H}_4\text{NHPO}_4$ , Ammonium phosphate; ammonii phosphas. Colorless; freely soluble.

$\text{H}_4\text{NC}_2\text{H}_3\text{O}_2$ , Ammonium acetate; ammonii acetas. A colorless salt contained in "Liquor Ammonii Acetatis."

$(\text{H}_4\text{N})_3\text{C}_6\text{H}_5\text{O}_7$ , Ammonium citrate; ammonii citras. Colorless; readily soluble.

$\text{H}_4\text{NC}_7\text{H}_5\text{O}_3$ , Ammonium salicylate; ammonii salicylas. White or colorless; soluble.

$\text{H}_4\text{NC}_7\text{H}_5\text{O}_2$ , Ammonium benzoate; ammonii benzoas. White, crystalline; readily soluble.

$\text{H}_4\text{NC}_5\text{H}_9\text{O}_2$ , Ammonium valerate (or valerianate); ammonii valerianas. Colorless, crystalline; freely soluble.

An "aromatic spirit of ammonia" containing ammonium carbonate and some volatile oils is also officinal. In England this is called "sal volatile," a title which is in other countries given to ammonium carbonate. The ammonium carbonate was formerly called "hartshorn salt;" the "ammonia water" or solution of ammonium hydroxide was called "spirit of hartshorn;" and ammonium chloride is commonly called "sal ammoniac" and "muriate of ammonia."

**807. General properties and reactions.** Ammonium salts are generally white or colorless and water-soluble. Ammonium bitartrate is, however, not freely soluble, and ammonium-platinum chloride is nearly insoluble. They are isomorphous with the salts of potassium.

They are volatile if their negative radicals are volatile, and vaporize without residue with or without previous decomposition.

On the addition of potassium hydroxide or sodium hydroxide to any ammonium salt, the odor of ammonia is at once developed, and the ammonia vapor may be detected, even if the amount be minute, by the white cloud formed when a glass rod moistened with diluted hydrochloric acid is held over the mixture.

Ammonium carbonate usually has a decided ammoniacal odor; but very hard, dry ammonium carbonate in perfect condition becomes nearly odorless when taken out of its container and left exposed to the air a short time.

The nitrate, acetate, iodide and valerate are deliquescent.

## CHAPTER LXVII.

### METALLIC SALTS OF THE ORGANIC ACIDS.

**808.** Many metallic salts formed with or by the organic acids are employed in pharmacy and medicine, and this book, although devoted to *inorganic* pharmaceutical chemistry, would be incomplete, indeed, if those salts should be omitted from it. They are, therefore, included.

**809. Acetates.** Acetic acid has the composition  $\text{HO.CO.CH}_3$ , which is, for the sake of convenience, written  $\text{HC}_2\text{H}_3\text{O}_2$ . It is the acid contained in vinegar and is extensively employed. It will be fully described in Part IV.

As all metallic acetates are water-soluble they may generally be prepared from acetic acid by neutralizing or saturating that acid with the metallic oxides, hydroxides or carbonates. The acid does not dissolve any of the common metals sufficiently readily to render the production of the acetates by that method practicable.

Sometimes acetates are made by metathesis between metallic salts, which is practicable whenever the bye-product is insoluble, as when sodium acetate is produced from lead acetate by double decomposition with sodium carbonate or sodium sulphate. But pure acetic acid is now manufactured from wood at a cost so small that the acetates are nearly always made from the acid.

The most common acetates include:

$\text{HC}_2\text{H}_3\text{O}_2$ , Hydrogen acetate, or acetic acid; acidum aceticum.

A colorless, volatile, pungent, sour liquid.

$\text{KC}_2\text{H}_3\text{O}_2$ , Potassium acetate; potassii acetat. A white, crystalline powder; deliquescent.

$\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ , Sodium acetate; sodii acetat. Colorless crystals, or a white granular crystalline powder. Efflorescent in warm, dry air. Freely soluble.

$\text{H}_4\text{NC}_2\text{H}_3\text{O}_2$ , Ammonium acetate; ammonii acetat. A colorless, crystalline, freely soluble salt. Contained in "liquor ammonii acetatis."

$\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$ , Magnesium acetate; magnesii acetat. A white, tenacious mass. Hygroscopic.

$\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ , Zinc acetate; *zinci acetas*. White crystals; somewhat efflorescent. Freely soluble.

$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ , Lead acetate; *plumbi acetas*. Colorless crystals, or a white, crystalline, granular salt. Readily soluble.

$\text{PbOHC}_2\text{H}_3\text{O}_2$ , Basic lead acetate; *plumbi subacetas*. A colorless salt contained in "*liquor plumbi subacetatis*."

$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ , Cupric acetate; *cupri acetas*. Dark green, transparent crystals. Soluble.

$\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$ , Ferric acetate; *ferri acetas*. Dark red-brown, amorphous. Contained in "*liquor ferri acetatis*."

The acetates are readily decomposed by dilute sulphuric acid and by other inorganic acids, acetic acid being given off, which is readily recognized by its peculiar and pronounced pungent odor. The acetates of the alkaline earth metals are hygroscopic; potassium acetate is deliquescent; many acetates gradually give off acetic acid when exposed to the air.

**810. Valerates**, or valerianates. Valeric acid, or valerianic acid, has the composition  $\text{HO.CO}(\text{CH}_2)_3\text{CH}_3$ , which is, for convenience, written  $\text{HC}_5\text{H}_9\text{O}_2$ . The acid is named after the plant *Valeriana*, in the root of which it was first found. It has a very strong valerian-like odor, which is also possessed in a less degree by its salts.

The most common valerates are:

$\text{HC}_5\text{H}_9\text{O}_2$ , Valeric acid; *acidum valerianicum*. A colorless, volatile liquid of a very strong characteristic odor.

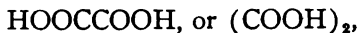
$\text{NaC}_5\text{H}_9\text{O}_2$ , Sodium valerate; *sodii valerianas*. Colorless, crystalline; readily soluble.

$\text{H}_4\text{NC}_5\text{H}_9\text{O}_2$ , Ammonium valerate; *ammonii valerianas*. Colorless, crystalline; deliquescent.

$\text{Zn}(\text{C}_5\text{H}_9\text{O}_2)_2 \cdot \text{H}_2\text{O}$ , Zinc valerate; *zinci valerianas*. White, crystalline; not very soluble.

$\text{Fe}(\text{C}_5\text{H}_9\text{O}_2)_3$ , Ferric valerate; *ferri valerianas*. Red, amorphous powder; insoluble.

Valerates have a tendency to give off valeric acid on exposure to the air. On the addition of dilute sulphuric acid to a valerate the valeric acid odor at once becomes strongly manifest.

**811. Oxalates.** Oxalic acid has the composition

which is conveniently written  $\text{H}_2\text{C}_2\text{O}_4$ . It is perhaps the strongest or most energetic of all organic acids, and it is noteworthy that the molecule of oxalic acid contains the carboxyl group,  $\text{CO}\cdot\text{OH}$ , twice, and consists of that alone, carboxyl being the atomic group characteristic of the organic acids.

Oxalic acid exists naturally in plants, but is manufactured from wood.

The following oxalates are common:

$\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ , Oxalic acid; acidum oxalicum. Colorless crystals. Readily soluble.

$\text{K}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ , Potassium oxalate; potassii oxalas. Colorless crystals. Soluble.

$\text{KHC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ , Acid potassium oxalate; potassii binoxalas. Colorless crystals, or a white, crystalline powder. called also "sal acetosellæ." Not freely soluble.

$(\text{H}_4\text{N})_2\text{C}_2\text{O}_4\cdot \text{H}_2\text{O}$ , Ammonium oxalate; ammonii oxalas. Colorless crystals; freely soluble.

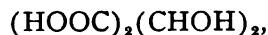
$\text{CaC}_2\text{O}_4$ , Calcium oxalate; calcii oxalas. White, quite insoluble powder.

$\text{Ce}_2(\text{C}_2\text{O}_4)_3\cdot 9\text{H}_2\text{O}$ , Cerous oxalate; cerii oxalas. An insoluble, white powder.

$\text{FeC}_2\text{O}_4\cdot \text{H}_2\text{O}$ , Ferrous oxalate; ferri oxalas. A sulphur-yellow, insoluble, crystalline powder.

The oxalates are prepared from oxalic acid.

Calcium oxalate is so completely insoluble in water that soluble oxalates and calcium salts are employed as reagents and precipitants for each other, except in acid solutions containing the stronger acids, in which calcium oxalate is soluble.

**812. Tartrates.** Tartaric acid has the composition

which is conveniently represented by the common formula  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ . The source of tartaric acid is the impure acid tartrate of potassium called "argols," or "crude tartar," which deposits from wines in the process of manufacture. Acid

tartrate of potassium is contained in the juice of "tart" grapes and some other fruits. Purified potassium bitartrate, or acid tartrate, is called "cream of tartar," *Cremor Tartari*.

The following tartrates are common:

$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ , Tartaric acid; *acidum tartaricum*. Colorless crystals, or a white powder, of an agreeable, strongly acid taste. Readily soluble.

$\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ , Potassium tartrate; *potassii tartras*. White, crystalline; readily soluble.

$\text{KHC}_4\text{H}_4\text{O}_6$ , Acid potassium tartrate; *potassii bitartras*. Cream of tartar. Colorless crystals or a white powder. very sparingly soluble.

$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ , Potassium-sodium tartrate; *potassii et sodii tartras*. Rochelle salt. Colorless crystals, or a white powder. Freely soluble.

$\text{NaC}_4\text{H}_4\text{O}_6$ , Sodium tartrate; *sodii tartras*. White, crystalline; readily soluble.

$\text{NaHC}_4\text{H}_4\text{O}_6$ , Acid sodium tartrate; *sodii bitartras*. Colorless crystals or white powder. Not freely soluble.

$(\text{H}_4\text{N})_2\text{C}_4\text{H}_4\text{O}_6$ , Ammonium tartrate; *ammonii tartras*. Colorless or white, crystalline; readily soluble.

$\text{H}_4\text{NHC}_4\text{H}_4\text{O}_6$ , Acid ammonium tartrate; *ammonii bitartras*. White or colorless, crystalline; not freely soluble.

$2\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ , Potassium-antimonyl tartrate; *antimoni et potassii tartras*. Called "tartrate of antimony and potassium," and "tartar emetic." Colorless or white crystals, or white powder. Soluble.

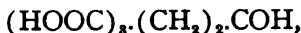
"Tartrate of iron and potassium," and "tartrate of iron and ammonium," in dark red scales, freely soluble in water, are official.

The tartrates are generally made from tartaric acid or from the acid tartrates of potassium or ammonium, except cream of tartar, from which the tartaric acid is prepared.

Solutions containing the alkali tartrates, including solutions of the tartrate of iron and potassium and tartrate of iron and ammonium, produce precipitates of acid tartrates on the addition of hydrochloric, sulphuric or nitric acid.

The alkali tartrates are decomposed at red heat, more readily when carbon is added, leaving a residue of alkali carbonate.

**813. Citrates.** The structure of citric acid is



represented by the common formula  $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ . The acid is obtained from the juice of lemons, limes and other fruits of the *Citrus* family.

These citrates are common:

$\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ , Citric acid; acidum citricum. Colorless crystals of an agreeable acid taste. Readily soluble.

$\text{K}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ , Potassium citrate; potassii citras. A white, granular powder. Readily soluble.

$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ , Normal sodium citrate; sodii citras. White, crystalline; soluble.

$\text{Na}_2\text{HC}_6\text{H}_5\text{O}_7$ , Di-sodium-hydrogen citrate. Readily soluble.

$\text{NaH}_2\text{C}_6\text{H}_5\text{O}_7$ , Sodium-di-hydrogen citrate. Readily soluble.

$(\text{H}_4\text{N})_3\text{C}_6\text{H}_5\text{O}_7$ , Ammonium citrate; ammonii citras. Colorless; readily soluble.

$\text{Li}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 4\text{H}_2\text{O}$ , Lithium citrate; lithii citras. White, deliquescent powder.

$\text{Mg}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ , Magnesium citrate; magnesii citras (normal). White powder; only partially soluble; decomposed by water.

$\text{MgHC}_6\text{H}_5\text{O}_7$ , Acid magnesium citrate. Colorless; soluble.

$\text{FeC}_6\text{H}_5\text{O}_7$ , Ferric citrate; ferri citras. Dark red, transparent scales; soluble.

$\text{BiC}_6\text{H}_5\text{O}_7$ , Bismuth citrate; bismuthi citras. White, granular powder; insoluble.

The water-soluble citrates as well as bismuth citrate are prepared from citric acid.

Bismuth citrate is readily soluble in ammonia water. Ferric citrate is only slowly but perfectly soluble in water; freely and easily soluble in a solution of ammonium citrate or on addition of a little ammonia to the water used to dissolve the ferric citrate. "Citrate of iron and ammonium" is commonly called "soluble citrate of iron" because it is so quickly soluble as compared with ferric citrate without ammonium citrate.

Citrates of iron and quinine and of iron and strychnine are also contained in the Pharmacopœia; also a soluble, scaled citrate of bismuth and ammonium.

Solutions of the alkali citrates dissolve ferric phosphate, pyrophosphate and hypophosphite, forming green or greenish solutions. The alkali citrates also form a green compound with ferric chloride. These iron compounds with the citrates are nearly free from the disagreeable, astringent, ferruginous or inky taste usually belonging to purely inorganic soluble iron salts.

**814. Lactates.** The structure of lactic acid is



which is commonly written  $\text{HC}_3\text{H}_5\text{O}_3$ . Lactic acid is the acid contained in sour milk and is formed by "lactic fermentation" of milk sugar, or of glucose.

The following lactates are officinal:

$\text{HC}_3\text{H}_5\text{O}_3$ , Lactic acid; acidum lacticum. The Pharmacopœia contains a solution of 75 per cent strength. It is a colorless, syrupy, acid liquid.

$\text{NaC}_3\text{H}_5\text{O}_3$ , Sodium lactate; sodii lactas. White powder; readily soluble.

$\text{Ca}(\text{C}_3\text{H}_5\text{O}_3)_2$ , Calcium lactate; calcii lactas. White or pale yellow powder. Soluble.

$\text{Mg}(\text{C}_3\text{H}_5\text{O}_3)_2$ , Magnesium lactate; magnesii lactas. White powder; soluble.

$\text{Zn}(\text{C}_3\text{H}_5\text{O}_3)_2$ , Zinc lactate; zinci lactas. White powder; soluble.

$\text{HgC}_3\text{H}_5\text{O}_2$ , mercurous lactate. Crimson, insoluble powder.

$\text{Fe}(\text{C}_3\text{H}_5\text{O}_3)_2$ , Ferrous lactate; ferri lactas. Pale greenish-yellow or yellowish-white powder; soluble.

All of these lactates are prepared from lactic acid.

When potassium permanganate is added to a mixture of equal volumes of lactic acid and sulphuric acid and the whole gently heated an odor of aldehyde is developed.

**815. Salicylates.** Salicylic acid has the structure



commonly written  $\text{HC}_7\text{H}_5\text{O}_3$ . It exists in certain plants,

as in *Spiraea ulmaria* and in *Gaultheria procumbens*. It may be made from the volatile oil of *Gaultheria*, which is methyl salicylate. The "oil of betula" also consists chiefly of methyl salicylate. But salicylic acid is manufactured on a larger scale from "carbolic acid," or phenol,  $C_6H_5OH$ .

The officinal salicylates are:

$HC_7H_5O_3$ , Salicylic acid; acidum salicylicum. A white, crystalline powder. Very sparingly soluble in water.

$2NaC_7H_5O_3 \cdot H_2O$ , Sodium salicylate; sodii salicylas. A white powder; very freely soluble.

$2LiC_7H_5O_3 \cdot H_2O$ , Lithium salicylate; lithii salicylas. White powder; deliquescent.

$Zn(C_7H_5O_3)_2 \cdot 3H_2O$ , Zinc salicylate; zinci salicylas. White powder; insoluble.

$Hg(C_7H_5O_3)_2$ , Mercuric salicylate; hydrargyri salicylas. White, insoluble powder.

$Fe(C_7H_5O_3)_3$ , Ferric salicylate; ferri salicylas. Purplish-black, insoluble powder.

$Bi(C_7H_5O_3)_3$ , Bismuth salicylate; bismuthi salicylas. Insoluble, white powder.

Salicylates of the alkali metals and alkaline-earth metals are soluble; those of the heavy metals insoluble. The water-soluble salicylates are prepared from salicylic acid; the others from sodium salicylate or from the acid.

**816. Phenolsulphonates.** These compounds are commonly called "sulpho-carbolates." Phenolsulphonic acid is



commonly written  $HC_6H_4SO_3$ . It is produced by the action of strong sulphuric acid upon phenol with the aid of long continued heat.

The metallic salts of pharmaceutical interest are para-phenol-sulphonates:

$NaC_6H_4SO_3 \cdot 2HO$ , Sodium phenolsulphonate; sodii phenolsulphonas. Colorless crystals; soluble.

$Ca(C_6H_4SO_3)_2$ , Calcium phenolsulphonate. White; soluble.

$\text{Ba}(\text{C}_6\text{H}_5\text{SO}_4)_2$ , Barium phenolsulphonate. White or colorless; soluble.

$\text{Zn}(\text{C}_6\text{H}_5\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ , Zinc phenolsulphonate; zinci phenolsulphonas. Called "zinci sulphocarbolas." Colorless, water-soluble crystals.

When strongly heated the phenolsulphonates decompose and give off vapors having the characteristic odor of phenol ("carbolic acid").

**817. Benzoates.** Benzoic acid has the structure  $\text{HOOC} \cdot \text{C}_6\text{H}_5$ , commonly written  $\text{HC}_7\text{H}_5\text{O}_2$ . It occurs naturally in benzoin and in some other balsamic resins and oleoresins. But benzoic acid is manufactured at present from toluol and from other substances.

The following benzoates are officinal:

$\text{HC}_7\text{H}_5\text{O}_2$ , Benzoic acid; acidum benzoicum. Minute white crystals of a silky lustre. Nearly insoluble in water.

$\text{NaC}_7\text{H}_5\text{O}_2 \cdot \text{H}_2\text{O}$ , Sodium benzoate; sodii benzoas. A white, amorphous powder; freely soluble.

$\text{LiC}_7\text{H}_5\text{O}_2$ , Lithium benzoate; lithii benzoas. White powder; readily soluble.

$\text{H}_4\text{NC}_7\text{H}_5\text{O}_2$ , Ammonium benzoate; ammonii benzoas. White, crystalline; readily soluble.

$\text{Ca}(\text{C}_7\text{H}_5\text{O}_2)_2$ , Calcium benzoate; calcii benzoas. White, crystalline; soluble.

$\text{Fe}(\text{C}_7\text{H}_5\text{O}_2)_3$ , Ferric benzoate; ferri benzoas. Reddish powder. Insoluble in water.

The water-soluble benzoates are made from benzoic acid; insoluble metallic benzoates are prepared from the sodium salt.

Natural benzoic acid has an agreeable benzoin-like odor, and the benzoates made from such benzoic acid have in a much less degree the same odor.

Artificial benzoic acid is odorless. When benzoic acid or a benzoate is heated with a large proportion of calcium hydroxide, freshly prepared, benzol is evolved.

**818. Oleates.** Oleic acid is  $\text{HC}_{18}\text{H}_{33}\text{O}_2$ . It is contained in most of the common fats, liquid and solid. Olive oil, almond oil, cotton seed oil, and many other fixed oils contain a very large proportion of *olein* or glyceryl oleate,  $\text{C}_3\text{H}_5(\text{C}_{18}\text{H}_{33}\text{O}_2)_3$ . But

these oils and fats contain also the glycerides or glyceryl salts of other fat acids, especially stearic acid.

The only water-soluble oleates are the "soaps." These are *soft soap*, or potassium oleate; and *hard soap*, or sodium oleate. The oleates of the heavy metals are "plasters," or plaster-like substances.

Oleic acid is obtained in a sufficiently pure condition from the "red oil" which is a crude bye-product gotten in the manufacture of candles.

Some of the metallic oleates are:

$\text{KC}_{18}\text{H}_{33}\text{O}_2$ , Potassium oleate. The chief constituent of soft soap, *sapo mollis*, which is also called "green soap," *sapo viridis*. A greenish-brown, or greenish-yellow, or brownish-yellow, soft, translucent, water-soluble soap.

$\text{NaC}_{18}\text{H}_{33}\text{O}_2$ , Sodium oleate. The chief constituent of hard soap, or "castile soap," or white olive oil soap, *sapo*, or *sapo durus*. It is also the principal constituent of all toilet soaps. Firm, white, forming a somewhat opaque or turbid solution with water.

$\text{Zn}(\text{C}_{18}\text{H}_{33}\text{O}_2)_2$ , Zinc oleate; *zinci oleas*. The chief constituent of the ordinary forms of pharmaceutical oleate of zinc, *oleatum zinci*. A soft, unctuous, white powder.

$\text{Pb}(\text{C}_{18}\text{H}_{33}\text{O}_2)_2$ , Lead oleate. The principal constituent of lead plaster. Nearly white.

$\text{Cu}(\text{C}_{18}\text{H}_{33}\text{O}_2)_2$ , Cupric oleate. Hard, green, plaster-like.

$\text{Hg}(\text{C}_{18}\text{H}_{33}\text{O}_2)_2$ , Mercuric oleate. The chief constituent of oleate of mercury, *oleatum hydrargyri*. A light yellowish-brown, soft ointment-like solid.

$\text{Fe}(\text{C}_{18}\text{H}_{33}\text{O}_2)_3$ , Ferric oleate. Brown-red, firm, plaster-like.

$\text{Al}(\text{C}_{18}\text{H}_{33}\text{O}_2)_3$ , Aluminum oleate. Firm, whitish, somewhat elastic.

$\text{Bi}(\text{C}_{18}\text{H}_{33}\text{O}_2)_3$ , Bismuth oleate. Firm, white.

The metallic oleates are generally prepared from oleic acid and the metallic oxides, or from sodium oleate by metathesis.

These compounds are decomposed by hydrochloric or sulphuric acid, oleic acid being formed.

The oleates are generally soluble in ether.



PART III.

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STOECHIOMETRY.



# STOECHIOMETRY.

## CHAPTER LXVIII.

### THE STOECHIOMETRY OF PROCESSES OF PRODUCTION.

**819.** By **stoichiometry** is meant the computation of the proportions of elements and compounds taking part in chemical reactions.

The student has seen that molecules of any one given kind have exactly the same composition, that molecules of different kinds have different composition or structure, and that all molecules are composed of atoms of which only a little over seventy distinct kinds are known, each kind having its own atomic weight. All molecular weights are accordingly the sums of the weights of the component atoms and their multiples.

We have also seen that atomic valence is governed by natural law and restricts the possible combinations of atoms within certain limits, and that the percentage composition of all common inorganic chemical compounds is known.

The molecular weights accepted by chemists are probably either quite correct or are simple multiples or aliquot parts of the correct ones. It is, therefore, practicable to construct chemical equations which lead to correct results in chemical operations, and stoichiometric calculations based upon correct chemical equations constitute the foundation of all practical applications of chemistry.

It is *possible* to know *something* of theoretical chemistry, and to even do *some* successful and correct laboratory work in chemistry by strictly obeying the directions laid down in reliable books, without possessing a thorough mastery of the construction and use of chemical equations and of stoichiometry; but the chemical work done by operators who can not of their own knowledge and skill write and balance chemical equations and make correct stoichiometric calculations must always be untrustworthy.

No other test of the true, actual working knowledge of chemistry possessed by any person claiming to be a pharmacist or a chemist is of greater importance than his ready command of

chemical equations and stoichiometry, for even the highest degree of care and manipulative skill in actual laboratory work must be defeated without it.

**820.** Stoichiometric calculations are based upon chemical equations and the atomic and molecular weights of the factors and products of the reactions represented by those equations. A sufficient number of examples will here be given to render the method clear to the student so that he may afterwards be able to solve other examples until he shall have had enough practice to be thoroughly grounded in this extremely important branch of chemical mathematics.

But the student should not forget that the exact proportions indicated by the chemical equations are not always the right ones in actual practice.

**821.** It has been pointed out elsewhere in this book that the relative masses of the factors of a reaction frequently have a decided influence upon its direction and extent, and also that partial reactions are rarely of practical use in processes employed for the production of chemicals. It is almost always necessary that the reactions shall be complete—that is, the materials employed, or at least one of them, must be completely decomposed or consumed, and to insure this result one of the factors or materials must generally be used in excess of the quantity theoretically required according to the equation.

**822.** In the exact neutralization of acids and of alkalies the precise proportions required by theory are in most cases used. But in other cases, as when certain acids are *saturated* with certain metals or metallic oxides, hydroxides or carbonates, the metal or its compound is often employed in larger proportion, and necessarily so. The quantity taken over and above that required for the formation of the product sought in such cases insures the saturation of the whole amount of the acid, and may be required further to prevent the formation of other compounds and the introduction of impurities into the product. Thus it is practicable to use zinc contaminated with other metals provided it be added in excess so that the acid may be saturated with zinc alone to the exclusion of the other metals, for zinc precipitates all metals of less strongly basic character.

**823.** Crystallizable salts of the heavy metals generally crystallize best from acid solutions, and salts of the alkali metals often

crystallize most advantageously from decidedly alkaline solutions. Hence exact neutralization in such cases is often purposely followed by the addition of a sufficiency of free acid or of alkali to insure the best attainable results.

**824.** Again, in the evaporation of solutions of salts of volatile acids or bases it is frequently necessary to add an excess of the acid or of the base, as the case may require, from time to time, to prevent the partial decomposition of the product, for if the salt be that of a volatile acid, such as acetic or valeric acid, free acid may be disengaged and dissipated which would render the product alkaline, and if the product be an ammonium salt it may become acid instead of neutral unless neutralized by the addition of more ammonia from time to time.

**825.** We have also learnt that in metatheses it rarely happens that both factors of the reaction are completely decomposed or consumed, and that in order to cause the complete decomposition of one of them the other must be used in excess.

**826.** For the reasons which we have just recapitulated it is of the utmost importance that the operator shall know the exact proportions required by theory, the strength or purity of the materials used, and which one of the materials must be employed in excess of the quantity required by the chemical equation.

**827.** The exact strength of acids, alkali solutions and other solutions, and the actual value of all other materials must be known, the quantity of moisture contained in salts and other compounds used must be taken into account, as well as the quantity of water lost from effloresced substances. The proportions of the materials as laid down in the working-formulas of pharmacopœias and other laboratory manuals, and the proportions called for by chemical equations, must, therefore, be changed whenever these circumstances require it.

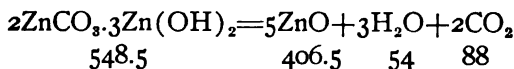
**828.** This brings us to a consideration of the atomic weights which should be employed. Shall we use the values based upon  $H=1$ , or those based upon  $Oxygen=16$ ? Shall we adopt the most nearly accurate determinations available, carrying out the decimals to the fullest extent, or shall the numbers be "rounded off;" and, if approximately correct values are permissible, how far may we safely round off the decimals of the atomic weights?

If the atomic weight of  $H$  is 1, then the atomic weight of  $O$  is 15.879; if the atomic weight of  $O$  is taken to be 16, then that of

H would be 1.008. Hence if we should assign to H the at. w. of 1, and to O that of 16, we would alter their true relations to the extent of about 0.8 per cent. This difference would have absolutely no practical bearing upon the results of actual laboratory operations, and I, therefore, recommend that it be ignored in order to simplify the arithmetical processes. If we assume that the atomic weight of hydrogen is 1 and that of oxygen 16, and then round off the numbers expressing the atomic weights of other elements within those limits (making them always not more than the number based on  $O=16$  and not less than the number based on  $H=1$ ), and if we, at the same time, avoid a disproportionate increase of the atomic weights of the heavy metals or a disproportionate decrease of the atomic weights of the alkali metals and the typical non-metallic elements, the approximate atomic weights thus obtained will be found far more convenient than the exact values, and the employment of these approximate atomic weights, as given in the table in Chapter IV, Vol. I, will afford thoroughly reliable results in all practical work, analytical as well as synthetical.

### 829. Examples in stoichiometry.

1. What quantity of zinc oxide can be obtained from 1 kilogram of zinc carbonate?



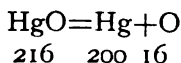
The total of the weights of the atoms in the  $2\text{ZnCO}_3.3\text{Zn}(\text{OH})_2$  is 548.5. The total of the molecular weights of the products, if the equation be correct, must, therefore, also be 548.5

(and  $406.5 + 54 + 88 = 548.5$ ).

Hence 549 Gm of zinc carbonate will furnish 407.5 Gm of zinc oxide. Then—

$$548.5 : 1000 :: 406.5 : x, \text{ and } x = 742 \text{ Gm.}$$

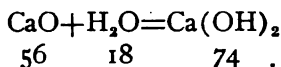
2. How much mercury is contained in 100 Gm of mercuric oxide?



As 216 Gm of mercuric oxide contains 200 Gm of mercury,

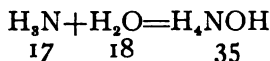
$X : 100 :: 200 : 216$ , and  $x=92.60$  Gm .

3. How much calcium hydroxide can be made out of 240 Gm of calcium oxide?



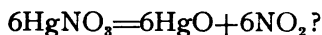
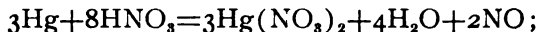
Ans.  $56 : 240 :: 74 : x$ , and  $x=317.14$  Gm .

4. The official ammonia water contains 10 per cent of  $\text{H}_3\text{N}$ ; what per cent of ammonium hydroxide does it contain?



Ans.  $17 : 35 :: 10 : x=20.59\%$ .

5. How much nitric acid of 68 per cent strength will be required to make red oxide of mercury out of 2 kilograms of mercury according to the equations:



From these equations it will be seen that 8 molecules of absolute nitric acid must be used to make 3 molecules of mercuric nitrate; but 6 molecules of mercurous nitrate can be produced by triturating 3 molecules of mercuric nitrate with 3 molecules (or atoms) of mercury. Hence we see that 6 atoms (or molecules) of mercury require 8 molecules of absolute (100%) nitric acid to make 6 molecules of mercuric oxide.

Assuming that the atomic weight of mercury is 200, the molecular weight of nitric acid 63, and the mol. w. of mercuric oxide 216, we find that 1200 weight units (or parts) of mercury can be turned into 1296 weight units (or parts) of mercuric oxide at the expense of 504 weight units of  $\text{HNO}_3$ . But 504 parts of nitric acid of 100% is equal to 756 parts of nitric acid of 68% strength.

Hence—

$$1200 : 2000 :: 756 : x = 1260 \text{ Gm.}$$

6. How much nitric acid of 63% strength is required to make red oxide of mercury out of two kilograms of mercury?

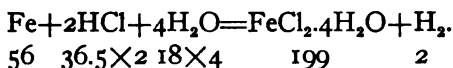
The student will observe that this example is the same as the preceding one in all respects except that the nitric acid is of 63% strength instead of 68%.

In the preceding example we found that 504 parts (or  $63 \times 8$ ) of nitric acid of 100% will be required. As the molecular weight of nitric acid is 63 it follows that 63 parts of 100% acid is equal to 100 parts of 63% acid, and (as 514 is  $63 \times 8$ ) 800 parts of 63% acid equals 514 parts of 100% acid.

Hence—

$$1200 : 2000 :: 800 : x = 1333.33 \text{ Gm}$$

7. How much (crystallized) ferrous chloride,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , can be produced (in water-solution) out of 1000 Gm of hydrochloric acid of 32% strength?



As 73 (or  $36.5 \times 2$ ) parts of absolute (100%) HCl will make 199 parts of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , and as 73 parts of hydrochloric acid of 100% strength is equal to 228.12 parts of hydrochloric acid of 32%, we have:

$$228.12 : 1000 :: 199 : x = 872.34 \text{ Gm.}$$

8. How much ferrous chloride,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , can be produced (in solution) out of 1000 Gm of hydrochloric acid of 36.4% strength?

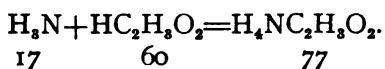
Here, as in the preceding example, we find that 199 parts of ferrous chloride can be made out of 73 parts of hydrochloric acid of 100% strength. But 73 (or  $36.4 \times 2$ ) parts of absolute acid is equal to 200 parts of an acid of 36.4% strength.

Hence—

$$200 : 1000 :: 199 : x = 995 \text{ Gm of } \text{FeCl}_2 \cdot 4\text{H}_2\text{O}.$$

9. Wanted 1000 Gm of a water-solution containing 10% of  $\text{H}_4\text{NC}_2\text{H}_3\text{O}_2$ . How much ammonia water of 28%  $\text{H}_3\text{N}$  and acetic acid of 36% will be required to make it. And how much additional water must be added?

The mol. w. of  $\text{H}_4\text{NC}_2\text{H}_3\text{O}_2$  is 77; that of  $\text{H}_3\text{N}$  is 17; and that of  $\text{HC}_2\text{H}_3\text{O}_2$  is 60.



Hence we must have 17 parts of absolute  $\text{H}_3\text{N}$  (or 60.7 parts of a 28% solution of it), and 60 parts of absolute acetic acid (or 166.7 parts of an acid of 36%), to make 77 parts of ammonium acetate (or 770 parts of a 10 per cent solution of it). Then to find the quantity of 28% ammonia solution required for 1000 Gm of the 10% solution of ammonium acetate, we have:

$$770 : 1000 :: 60.7 : x = 78.8 \text{ Gm.},$$

and to find the quantity of acetic acid of 36%:

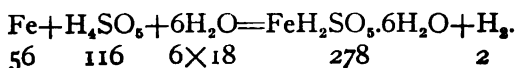
$$770 : 1000 :: 166.7 : x = 216.2 \text{ Gm.}$$

Hence 78.8 Gm of ammonia solution of 28%, 216.2 Gm acetic acid of 36%, and 705 Gm of water are required to make 1000 Gm of a 10% solution of ammonium acetate.

10. How much ammonia solution containing 17% of absolute  $\text{H}_3\text{N}$ , acetic acid containing 60% of absolute  $\text{HC}_2\text{H}_3\text{O}_2$ , and water will be required to make 1000 Gm of a 7.7% solution of ammonium acetate?

From the equation in the preceding example it was seen that 17 parts of absolute  $\text{H}_3\text{N}$  and 60 parts of absolute acetic acid make 77 parts of ammonium acetate. Hence the answer to this problem must be that 100 Gm of ammonia solution containing 17 per cent of  $\text{H}_3\text{N}$  and 100 Gm of an acetic acid solution containing 60 per cent of  $\text{HC}_2\text{H}_3\text{O}_2$  must, together with 800 Gm of water, make 1000 Gm of a solution containing 7.7 per cent of ammonium acetate.

11. How much ferrous sulphate represented by the formula  $\text{FeH}_2\text{SO}_6 \cdot 6\text{H}_2\text{O}$  will be contained in a solution made of 1160 Gm of absolute monometasulphuric acid ( $\text{H}_4\text{SO}_6$ ), saturated with iron [with sufficient water]?

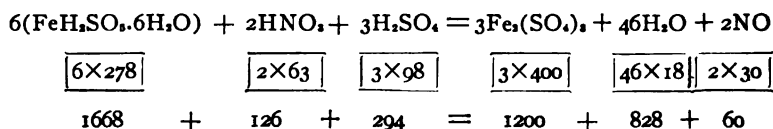


As all of the sulphuric acid will be consumed and 560 Gm of metal is required, the quantity of ferrous monometasulphate with 6 molecules of water (ordinary crystallized ferrous sulphate) formed out of the 1160 Gm of acid will be 2780 Gm.

[About 5000 Gm of water must also be used to dissolve the salt formed in order that the reaction may proceed with ease.]

12. How much ferrous sulphate,  $\text{FeH}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , sulphuric acid containing 92.5 per cent of  $\text{H}_2\text{SO}_4$ , nitric acid containing 68% of  $\text{HNO}_3$ , and water, will be required to make 1000 Gm of a solution containing 28.7% of ferric sulphate,  $\text{Fe}_2(\text{SO}_4)_3$ ?

The chemical equation is:



Thus it requires 1668 Gm of ferrous sulphate, 294 Gm of absolute  $\text{H}_2\text{SO}_4$ , and 126 Gm of absolute nitric acid to make 1200 Gm of  $\text{Fe}_2(\text{SO}_4)_3$ , and the factors will at the same time form 828 Gm of water. But we want only 287 Gm of  $\text{Fe}_2(\text{SO}_4)_3$ . Then—

$$1200 : 287 :: \begin{cases} 1668 : x = 398.93 \text{ Gm ferrous sulphate} \\ 294 : x = 70.31 \text{ Gm absolute } \text{H}_2\text{SO}_4 \\ 126 : x = 30.13 \text{ Gm absolute } \text{HNO}_3 \end{cases}$$


---

499.37 Gm

These materials will form

287	Gm	$\text{Fe}_2(\text{SO}_4)_3$
198	Gm	water
14.37	Gm	NO
<hr style="width: 50%; margin-left: 0;"/>		
499.37	Gm	

But 70.31 Gm of absolute  $\text{H}_2\text{SO}_4$  is equivalent to 76.01 Gm of a sulphuric acid containing 92.5 per cent of  $\text{H}_2\text{SO}_4$ ; and 30.13 Gm of absolute nitric acid is equivalent to 44.31 Gm of an acid containing 68% of  $\text{HNO}_3$ .

We shall, therefore, require, to make 1000 Gm of a 28.7 per cent solution of  $\text{Fe}_2(\text{SO}_4)_3$ :

398.93 Gm ferrous sulphate  
 76.01 Gm sulphuric acid of 92.5%  
 44.31 Gm nitric acid of 68%  
 480.75 Gm of water

---

1000.00 Gm containing 287 Gm of  $\text{Fe}_2(\text{SO}_4)_3$ .

13. How much ferrous sulphate,  $\text{FeH}_2\text{SO}_5 \cdot 6\text{H}_2\text{O}$ , and how much sulphuric acid containing 98 per cent of  $\text{H}_2\text{SO}_4$  and nitric acid containing 63 per cent of  $\text{HNO}_3$ , and how much water, will be required to make 1000 Gm of a solution containing 40 per cent of  $\text{Fe}_2(\text{SO}_4)_3$ ?

From the chemical equation given in the preceding example we found that—

1668 Gm ferrous sulphate  
 294 Gm absolute  $\text{H}_2\text{SO}_4$  and  
 126 Gm absolute  $\text{HNO}_3$

---

2088 Gm

will form 1200 Gm  $\text{Fe}_2(\text{SO}_4)_3$   
 828 Gm water, and  
 60 Gm NO

---

2088 Gm

We want only 400 Gm of  $\text{Fe}_2\text{SO}_4$ , which is one-third of 1200. Hence we shall require

$$\frac{1668}{3} = 556 \text{ Gm of ferrous sulphate.}$$

$$\frac{294}{3} = 98 \text{ Gm of absolute } \text{H}_2\text{SO}_4$$

$$\frac{126}{3} = 42 \text{ Gm of absolute } \text{HNO}_3$$

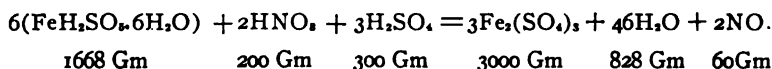
But 98 Gm of absolute  $\text{H}_2\text{SO}_4$  is equivalent to 100 Gm of 98% acid; and 42 Gm of absolute  $\text{HNO}_3$  is equivalent to 66.67 Gm of an acid containing 63% of  $\text{HNO}_3$ . Hence we shall get the final answer:

556	Gm of ferrous sulphate,
100	Gm of 98% sulphuric acid ( $\text{H}_2\text{SO}_4$ ),
66.67	Gm of 63% nitric acid ( $\text{HNO}_3$ ),
277.33	Gm of water.

---

1000.00 Gm containing 400 Gm of  $\text{Fe}_2(\text{SO}_4)_3$ .

14. This problem (13) may be more expeditiously solved if the strength of the solutions (the acids and the solution of ferric sulphate) bear a simple relation to the molecular weights of the substances contained in them, as we shall now show. The molecular weight of sulphuric acid,  $\text{H}_2\text{SO}_4$ , is 98; hence it is most convenient to use an acid containing 98 per cent of  $\text{H}_2\text{SO}_4$ , so that 100 Gm of the acid will be required for each molecule called for by the equation. The most convenient nitric acid is one of 63 per cent strength, because the molecular weight of  $\text{HNO}_3$  is 63. As the molecular weight of  $\text{Fe}_2(\text{SO}_4)_3$  is 400 we will find that a solution of 40 per cent strength is the most convenient one of that compound. The equation will then be written as follows:

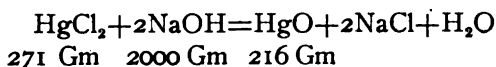


We take 200 Gm of nitric acid of 63% because 2 molecules are required; we take 300 Gm of sulphuric acid of 98% because 3 molecules are required of that, and we get 3000 Gm of solution of ferric sulphate because 3 molecules of it are produced, according to the equation.

Then, as we desire to make only 1000 Gm of the iron solution, we divide all the numbers by 3.

15. The mol. w. of  $\text{HgO}$  is 216; that of  $\text{NaOH}$  is 40; and that of  $\text{HgCl}_2$  is 271. What quantities are required of the

mercuric chloride and of a 4% solution of sodium hydroxide to make 500 Gm of precipitated mercuric oxide?



Then—

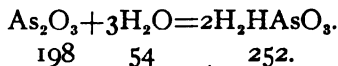
$$216 : 500 :: \begin{cases} 271 : x = 627 \text{ Gm of HgCl}_2 \\ 2000 : x = 4630 \text{ Gm of sol. of NaOH.} \end{cases}$$

But we know that the NaOH must be *in excess*; hence we add a little over 5 per cent to the quantity of the solution used, making it 4900 Gm instead of 4630 Gm.

16. What would be the proportions required of  $\text{HgCl}_2$  and of a 4% solution of NaOH to make precipitated  $\text{HgO}$ ?

Ans. 5 parts of  $\text{HgCl}_2$  and 39 parts of the solution to make 3.97 parts of  $\text{HgO}$ .

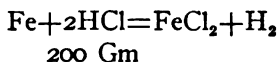
17. How much arsenous acid is contained in a solution made of 198 Gm of arsenous oxide and 20 liters of water?



Ans. 252 Gm.

18. How much hydrochloric acid of 36.5% strength (containing 36.5% of absolute  $\text{HCl}$ ) is necessary to form the quantity of ferrous chloride ( $\text{FeCl}_2$ ) required to produce 1000 Gm of a solution containing 32.5 per cent of  $\text{FeCl}_3$  (or 54.1 per cent of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ )?

The molecule of ferric chloride and the molecule of ferrous chloride each contains but one iron atom; hence one molecule of ferrous chloride will form one molecule of ferric chloride. The molecule of ferrous chloride contains 2 chlorine atoms, but the hydrochloric acid contains but one. The molecular weights are:  $\text{HCl} = 36.5$  and  $\text{FeCl}_3 = 162.5$ . But 162.5 is one-half of 325. Hence—



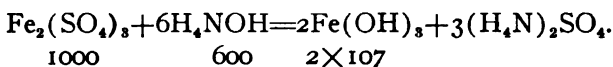
and one molecule of  $\text{FeCl}_2$  furnishes one molecule of  $\text{FeCl}_3$   
162.5 Gm.

so that to make 1000 Gm of a solution containing 325 Gm of  $\text{FeCl}_3$  it will be necessary to use the ferrous chloride produced by 400 Gm of hydrochloric acid of 36.5% strength.

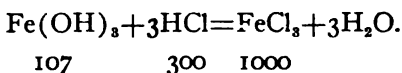
19. How much solution of ferric sulphate of 40% strength, ammonia water containing 35% of  $\text{H}_4\text{NOH}$ , and hydrochloric acid containing 36.5% of  $\text{HCl}$  will be required to make 1000 Gm of a solution containing 16.25 per cent of  $\text{FeCl}_3$ ?

(Mol. w. of  $\text{Fe}_2(\text{SO}_4)_3=400$ ; mol. w. of  $\text{H}_4\text{NOH}=35$ ; mol. w. of  $\text{HCl}=36.5$ ; and mol. w. of  $\text{FeCl}_3=162.5$ .)

First—



Then—



These equations show that 500 Gm of the solution of ferric sulphate will furnish the quantity of ferric hydroxide required to produce 1000 Gm of the solution of ferric chloride containing 16.25 per cent of  $\text{FeCl}_3$ , and that the quantity of ammonia solution necessary to precipitate the ferric hydroxide from the solution of ferric sulphate is theoretically 300 Gm., and the quantity of hydrochloric acid required to dissolve that ferric hydroxide to form the chloride must also be 300 Gm.

20. How much solution of  $\text{KOH}$  of 5 per cent strength must be taken to contain 56 Gm of  $\text{KOH}$ ? (The mol. w. of  $\text{KOH}$  is 56.)

21. What quantity of solution of  $\text{NaOH}$  of 5 per cent strength contains 40 Gm of  $\text{NaOH}$ ? (The mol. w. of  $\text{NaOH}$  is 40.)

22. How much hydrochloric acid of 31.9 per cent strength equals 1000 Gm of an acid containing 36.5 per cent of absolute  $\text{HCl}$ ?

23. By what number must 1 kilogram of hydrochloric acid of 31.9 per cent strength be multiplied to find the corresponding quantity of an acid of 36.5 per cent?

24. By what number must 2 kilograms of hydrochloric acid of 36.5 per cent strength be multiplied to find the corresponding quantity of an acid of 31.9 per cent?

25. How much hydrochloric acid of 36.5% equals 500 Gm of an acid of 31.9%?

26. How much hydrochloric acid of 31.9% equals 400 Gm of an acid of 36.5%?

27. By what co-efficient must any number of grams of nitric acid of 63 per cent strength be multiplied to find the corresponding number of grams of a nitric acid of 68 per cent strength?

28. The strength of the official acetic acid is 36 per cent. The molecular weight of  $\text{HC}_2\text{H}_3\text{O}_2$  is 60. What co-efficient must be used to find the number of grams of acetic acid of 36% strength which corresponds to or contains 60 Gm of absolute acetic acid?

29. If 98 Gm. of absolute  $\text{H}_2\text{SO}_4$  is required for a given reaction, how much sulphuric acid of 92.5 per cent strength must be employed? Or, in other words, how much sulphuric acid of 92.5% must you take to have 98 Gm of absolute acid?

30. How many times is 92.5 contained in 98, and what co-efficient should be used by which to multiply any quantity of sulphuric acid of 98% to find the corresponding quantity of acid of 92.5%?

31. How many times is 98 contained in 92.5, and what co-efficient must be used to multiply any quantity of sulphuric acid of 92.5% strength to find the corresponding quantity of acid of 98%?

32. How many times is 1.0594 contained in 1? And how many times is 0.9439 contained in 1? What is the reciprocal of 1.0594? And what is the reciprocal of 0.9439?

33. By what co-efficient should a given quantity of sulphuric acid of 100 per cent strength be multiplied to find the corresponding quantity of sulphuric acid of 98%? Of 96%? Of 92.5%?

34. By what co-efficient should a given quantity of sulphuric acid of 92.5% strength be multiplied to find the corresponding quantity of absolute acid?

35. How many times is 100 contained in 92.5? And how many times is 92.50 contained in 100?

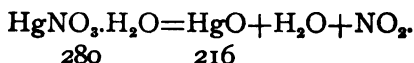
36. Having found from the chemical equation that the quantity of absolute sulphuric acid required for a certain reaction is 98 weight units, how many weight units of sulphuric acid of 96% strength must be taken?

37. The quantity of absolute hydrochloric acid required for a given reaction is 36.5 Gm; what number of Gm of hydrochloric acid of 31.9% strength contains that 36.5 Gm of absolute  $\text{HCl}$ ?

38. What quantity of nitric acid of 68 per cent strength con-

tains 63 Gm of absolute nitric acid? And what quantity of nitric acid of 63% strength contains 63 Gm of absolute nitric acid? By what number must 63 Gm of absolute acid be multiplied in order to find the corresponding number of Gm of 68% acid?

39. I have 280 Gm of mercurous nitrate ( $\text{HgNO}_3 \cdot \text{H}_2\text{O}$ ), and I wish to convert all of it into mercuric oxide by heat. How much product will I obtain?



Ans. 216 Gm .

How many times is 280 contained in 216? By what coefficient must any quantity of  $\text{HgNO}_3 \cdot \text{H}_2\text{O}$  be multiplied to find the quantity of  $\text{HgO}$  which it will yield?

40. Ferric acetate has the formula  $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$  and the molecular weight 233. The atomic weight of iron is 56. How many times is 233 contained in 56? And how many times is 56 contained in 233?

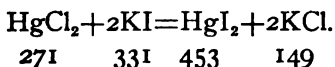
By what coefficient must any quantity of ferric acetate be multiplied to find the corresponding quantity of iron (or the quantity of iron contained in it)?

By what coefficient must any quantity of iron be multiplied to find how much ferric acetate contains that quantity of iron?

41. Mercuric chloride is  $\text{HgCl}_2$ , and has the molecular weight

271. Mercuric iodide is  $\text{HgI}_2$  with the mol. w. 453.

Mercuric iodide is prepared from mercuric chloride:



How many times is 271 contained in 453? And 453 in 271?

By what number must any quantity of  $\text{HgCl}_2$  be multiplied to find how much mercuric iodide can be made from it? How much mercuric iodide can be made out of 271 Gm of  $\text{HgCl}_2$ ?

42. A certain solution contains 50 per cent of  $\text{Fe}_2\text{Cl}_6$ . How many per cent of  $\text{FeCl}_3$  does it contain?

43. Crystallized ferric chloride is  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . We have a water-solution containing 200 Gm of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . To what weight must the whole solution be evaporated in order to form a solid crystalline cake on standing?

44. What is the theoretical yield of  $\text{H}_3\text{N}$  from 1 kilogram of  $\text{H}_4\text{NCl}$ ?

45. Magnesium carbonate is  $(\text{HO})_2\text{Mg}_6(\text{CO}_3)_4$ . Magnesia is  $\text{MgO}$ .

How much magnesia can be made out of 1 kilogram of the carbonate?

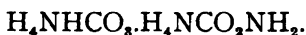
By what coefficient must any quantity of magnesia be multiplied to find its equivalent of magnesium carbonate?

By what coefficient must any quantity of magnesium carbonate be multiplied to find its equivalent of magnesia?

46. Zinc carbonate is  $(\text{HO})_6\text{Zn}_5(\text{CO}_3)_2$ . Zinc oxide is  $\text{ZnO}$ . Zinc acetate is  $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ .

How much zinc acetate can be made from 100 Gm of the carbonate? From 100 Gm of the oxide?

47. Ammonium carbonate has the composition



When acetic acid is neutralized with it all of the nitrogen of the ammonium carbonate enters into the formation of the ammonium acetate produced. How much ammonium acetate can be made out of 3 kilograms of acetic acid of 60 per cent strength by neutralizing it with ammonium carbonate, and how much ammonium carbonate will be required? And how much ammonium acetate can be made out of 3 kilograms of acetic acid of 60 per cent strength if the acid is neutralized with ammonia water instead of ammonium carbonate?

48. We have some sodium carbonate which has partially effloresced from exposure. Upon making sodium acetate out of it we find that 900 Gm neutralizes 4000 Gm of acetic acid of 36 per cent strength. How much water of crystallization did the sodium carbonate used contain?

Give the answer in molecules, and also in per cent.

49. We make ferric hydroxide from 2 kilograms of a solution containing 28.7 per cent of  $\text{Fe}_2(\text{SO}_4)_3$ , and after washing it thoroughly we put it into a press cloth and squeeze the water out of it until the weight of the press cake is reduced to just 1400 Gm. How much water is left in it?

50. How much  $\text{CO}_2$ , by weight and by volume, can be made from 10 kilos of chalk? And how much water at  $0^\circ$  can be saturated with that gas under a pressure of six atmospheres?

51. How much manganous chloride will be formed and how much acid will be consumed in making enough chlorine out of manganese dioxide and hydrochloric acid to saturate one liter of water?

52. How much oxygen is liberated from 100 Gm of a 3 per cent solution of  $\text{H}_2\text{O}_2$  when the dioxide is completely reduced to monoxide?

53. How much sulphurous acid is contained in a water-solution of  $\text{SO}_2$  the strength of which is expressed by 6.4 per cent of the dioxide?

54. How much potassium carbonate will be obtained by heating 100 Gm of the bicarbonate?

55. What proportions of copper sulphate and lead nitrate are required to make copper nitrate; and how much of each must be used to make 1 kilogram of the product?

56. How many Gm of ferric hydroxide will be obtained from 1 kilogram of a solution containing 28.7 per cent of  $\text{Fe}_2(\text{SO}_4)_3$  by complete precipitation with ammonia?

57. How many Gm of ferric hydroxide will be obtained from 1 kilogram of a solution containing 63 per cent of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  by complete precipitation with ammonia?

58. How much iron is contained in 100 Gm of a solution containing 10 per cent of  $\text{Fe}(\text{NO}_3)_3$ ?

59. How much ferric hydroxide corresponds to 1 Gm of iron?

60. How much  $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$  must be contained in 4 kilograms of a solution of that salt in order to make the solution correspond to 5 per cent of metallic iron?

61. What is the percentage of iron in a solution containing 32.5% of  $\text{FeCl}_3$ ?

And in a solution containing 20 per cent of  $\text{Fe}_2(\text{SO}_4)_3$ ?

62. What is the percentage of iron in a mixture made of 100 ml solution of ferric chloride having the specific weight 1.387 and containing 63 per cent of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , and 300 ml of alcohol of the sp. w. 0.820?

63. What is the percentage of As in a solution representing 1% of  $\text{As}_2\text{O}_3$ ?

In a solution representing 1 per cent of  $\text{Na}_2\text{HAsO}_4$ ?

In a solution representing 1 per cent of  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ?

In a solution representing 1.677 per cent of  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ?

In a solution representing 1% of  $\text{AsI}_3$ ?

## CHAPTER LXIX.

### THE STOECHIOMETRY OF VOLUMETRIC PROCESSES.

**830.** A volumetric test-solution is a solution of a reagent whereby the quantity of a given constituent contained in another solution can be accurately determined. All volumetric reactions are complete reactions, i. e., at least one of the factors of such reactions is completely consumed. It is because they proceed to completion that these reactions can be depended upon to indicate the exact quantity of the substance tested for.

"Normal" volumetric test-solutions are so made that the number of Grams of the reagent contained in one liter of the solution expresses the molecular weight of that reagent divided by the number of valence units presented by each of the two radicals or ions of the molecule, except in cases where the test solution is used as an oxidizing or reducing agent, in which case the molecular weight (or the atomic weight if the reagent be an element) is divided by the number of units of polarity-value lost or gained by the whole number of atoms of the oxidizing or reducing element contained in one molecule of the reagent.

**831.** A normal test-solution is designated by the expression  $\frac{N}{1}$ ; a decinormal or one-tenth normal solution is designated by  $\frac{N}{10}$ , and a centinormal or  $\frac{1}{100}$  normal solution by  $\frac{N}{100}$ ; a test-solution twice the strength of the normal, or a so-called "double-normal solution" is designated by  $\frac{2}{N}$ , and a half-strength normal or "seminormal solution" by  $\frac{N}{2}$ .

**832.** Volumetric test-solutions of reagents which do not undergo oxidation or reduction when used, are so prepared that equal volumes of different solutions (or volumes bearing the simplest possible proportions to each other) have the same exchangeable value in metatheses. Their exchangeable value is measured in the units of ordinary valence ( $H=1$ ), and the solutions are **chemical equivalents** when normal. Thus, 1 ml of normal hydrochloric acid corresponds to and exactly neutralizes 1 ml of normal solution of KOH, or 100 ml of centinormal solution of KOH, or 1 ml of normal NaOH solution, or it will pre-

precipitate the silver from exactly 10 ml of decinormal silver nitrate solution. One ml of normal sulphuric acid is exactly the equivalent of 1 ml of normal hydrochloric acid, for the normal test-solution of  $\text{H}_2\text{SO}_4$  contains only 49 Gm of the absolute acid (one-half of its mol. weight) in each liter, whereas the normal test-solution of  $\text{HCl}$  contains 36.4 Gm of the absolute acid (its whole mol. weight) in each liter, because the  $\text{SO}_4$  is a dyad ion while  $\text{Cl}$  is a monad ion, and the object is to make equal volumes of equal exchangeable value in chemical reactions.

One ml of normal sodium hydroxide exactly neutralizes 1 ml of normal hydrochloric acid, or 1 ml of normal sulphuric acid, or 1 ml of normal oxalic acid solution, or 10 ml of decinormal oxalic acid solution.

**833.** Decinormal *iodine* solution contains 12.65 Gm of iodine in each liter because the atomic weight of  $\text{I}$  is 126.5 and it is a monad. When it is used as a volumetric reagent, each atom of iodine loses one unit of polarity-value because it is reduced from a polarity-value of 0 to one of  $-1$ .

Each ml of decinormal solution of *sodium thiosulphate* decolorizes exactly 1 ml of decinormal solution of iodine, for each molecule of  $\text{Na}_2\text{SO}_3\text{S}$  reacts with 1 atom of iodine, the composition of crystallized sodium thiosulphate is  $\text{Na}_2\text{SO}_3\text{S} \cdot 5\text{H}_2\text{O} = 248$ , the atomic weight of iodine is 126.5, and 1 ml of decinormal iodine solution contains 0.01265 Gm of iodine, while 1 ml of decinormal solution of sodium thiosulphate contains 0.0248 Gm of that salt. When these two solutions are used together the 1 unit of polarity-value lost by each atom of iodine is taken up by a part of the sulphur of the  $\text{Na}_2\text{SO}_3\text{S}$  (see Par. 441, Ex. 54).

"Decinormal volumetric solution of *potassium permanganate*" contains 3.16 Gm of the salt in each liter. It is so prepared because the mol. weight of the compound is 158, and  $2\text{KMnO}_4 = 316$  (or  $158 \times 2$ ) will furnish 10 units of oxidation when used as an oxidizing agent in the presence of free acids, and in order to get a solution of which 1 ml will exactly correspond to and reduce 1 ml. of decinormal volumetric solution of oxalic acid it is evident that one-fifth of 158 Gm (or one-tenth of 316 Gm) of  $\text{KMnO}_4$  must be contained in each liter of a *normal* solution.

The decinormal volumetric test-solution of *potassium dichromate* contains 0.0049 Gm of  $\text{K}_2\text{Cr}_2\text{O}_7$  in each ml. The mol. w. of  $\text{K}_2\text{Cr}_2\text{O}_7$  is 294. Each molecule gives up six units of polarity-

value; hence one-sixth of 294 Gm of  $K_2CrO_7$  must be contained in each liter of a *normal* volumetric solution.

It will be seen that 1 ml of decinormal solution of potassium dichromate has exactly the same oxidizing power as 1 ml of decinormal solution of potassium permanganate, or as 1 ml of decinormal solution of iodine, so that these three oxidizing agents are exact equivalents, volume for volume, which, as we have seen, is in strict conformity to the principle upon which volumetric solutions are prepared.

Decinormal volumetric solution of *oxalic acid* is the exact equivalent of decinormal sulphuric acid when used in alkalimetric determinations; when used as a reducing agent it is the exact equivalent of decinormal volumetric solution of sodium thiosulphate.

The volumetric test-solutions, therefore, illustrate most perfectly the applications of stoichiometry.

#### EXAMPLES IN THE STOECHEOMETRY OF VOLUMETRIC DETERMINATIONS NOT INVOLVING OXIDATION AND REDUCTION.

##### 834. Normal volumetric solution of sulphuric acid.

$H_2SO_4=98$ . Each ml  $=0.049$  Gm

1. How much dry  $H_3N$  is represented by an ammonia solution which requires 24 ml of the normal solution of sulphuric acid for exact neutralization?

2. What per cent of KOH is contained in a solution 21 Gm of which requires 75 ml of normal solution of  $H_2SO_4$  for neutralization?

3. How many ml of normal solution of  $H_2SO_4$  will be neutralized by 1 Gm of  $NaHCO_3$ ?

4. How much potassium bicarbonate will neutralize 27 ml of normal V.S. of  $H_2SO_4$ ?

5. What is the per cent of  $H_3N$  in an alcoholic solution of ammonia of which 3.4 Gm neutralizes 25 ml of  $\frac{N}{1}$  V.S. of  $H_2SO_4$ ?

6. What per cent of  $HOPbC_2H_3O_2$  is contained in a solution of which 14 Gm requires 25 ml of  $\frac{N}{1}$  V.S. of  $H_2SO_4$  for complete precipitation (as indicated by the discharge of the color of methyl-orange T.S.)?

7. If 1.62 Gm of  $K_2C_6H_5O_7 \cdot H_2O$  be thoroughly ignited at red heat to convert it into  $K_2CO_3$ , how much  $\frac{N}{1}$  V.S. of  $H_2SO_4$  will be required to exactly neutralize to residue (dissolved in water)?

8. How much  $Li_2CO_3$  will be obtained by the complete ignition of 5 Gm of lithium salicylate,  $LiC_7H_5O_3$ ? And how much  $\frac{N}{1}$  V.S. of  $H_2SO_4$  will be required to neutralize that  $Li_2CO_3$ ?

9. How many Gm of  $H_4NHCO_3 \cdot H_4NCO_2NH_2$  must be contained in a solution of which 15.7 Gm neutralizes 10 ml of  $\frac{N}{1}$  V.S. of  $H_2SO_4$ ?

**835. Normal volumetric solution of oxalic acid.**

$H_2C_2O_4 \cdot 2H_2O = 126$ . Each ml = 0.063 Gm

1. How much  $KHCO_3$  will be required to neutralize 100 ml of this solution?

2. What per cent of  $NaOH$  is contained in a solution of which 10 Gm neutralizes 25 ml of  $\frac{N}{1}$  V.S. of  $H_2C_2O_4 \cdot 2H_2O$ ?

*Decinormal Solution.*

3. What is the per cent of  $Ca(OH)_2$  in a solution 30 Gm of which requires 18 ml of  $\frac{N}{10}$  V.S. of oxalic acid for complete precipitation?

4. How much  $K_2CO_3$  is contained in a potassium iodide of which a solution containing 10 Gm of the  $KI$  requires 1 ml of  $\frac{N}{10}$  V.S. of oxalic acid for neutralization (so as to prevent coloration with a drop of phenolphthalein T.S.)?

**836. Potassium hydroxide normal volumetric solution.**

$KOH = 56$ . Each ml = 0.056 Gm

1. How much  $H_3C_6H_5O_7 \cdot H_2O$  is required to exactly neutralize 30 ml of this solution?

2. What per cent of absolute  $HC_2H_3O_2$  is contained in a solution of which 1.5 Gm neutralizes 25 ml of  $\frac{N}{1}$  V.S. of  $KOH$ ?

3. How many ml of  $\frac{N}{1}$  V.S. of  $KOH$  is required to neutralize 5.86 Gm of a mixture of equal parts by weight of the official diluted hydrobromic and hydrochloric acids?

4. How much water must be added to an acetic acid of which 5 Gm neutralizes 50 ml of  $\frac{N}{1}$  V.S. of  $KOH$ , in order to reduce its strength to 36%?

5. If a solution of cream of tartar requires 10 ml of  $\frac{N}{1}$  V.S. of KOH for exact neutralization how many Gm of  $\text{KHC}_4\text{H}_4\text{O}_6$  must be contained in that solution?

6. How many ml of  $\frac{N}{1}$  V.S. of KOH will be required to neutralize 5 Gm of an 80% solution of  $\text{HC}_3\text{H}_5\text{O}_3$ ?

**837. Normal volumetric test-solution of sodium hydrozide.**

$\text{NaOH}=40$ . Each ml  $=0.04$  Gm

1. How much  $\frac{N}{1}$  V.S. of NaOH is required to form  $\text{Na}_2\text{HPO}_4$  with 9.8 Gm of a 15% solution of  $\text{H}_3\text{PO}_4$  as indicated by phenolphthalein? And how much to form  $\text{NaH}_2\text{PO}_4$  with 9.8 Gm of a 10% solution of  $\text{H}_3\text{PO}_4$ , as indicated by methyl-orange?

2. What is the per cent strength of a sulphuric acid 9.8 Gm. of which exactly neutralizes 10 ml of  $\frac{N}{1}$  V.S. of NaOH?

**838. Decinormal V.S. of sodium chloride.**  $\text{NaCl}=58.4$ . Each ml  $=0.00584$  Gm

What per cent of silver is contained in a solution of silver nitrate 10 Gm of which is exactly precipitated by 20 ml of  $\frac{N}{10}$  V.S. of NaCl?

**839. Decinormal V.S. of silver nitrate.**  $\text{AgNO}_3=170$ . Each ml  $=0.017$  Gm

1. What is the per cent strength of a dilute hydrocyanic acid 3 Gm of which requires exactly 33.33 ml of  $\frac{N}{10}$  V.S. of  $\text{AgNO}_3$  for complete precipitation?

2. How much  $\frac{N}{10}$  V.S. of  $\text{AgNO}_3$  is required for the complete precipitation of 3 Gm of a dilute hydrocyanic acid containing exactly 2 per cent of HCN?

3. How much pure LiBr is contained in 3 Gm of solution requiring 34 ml of  $\frac{N}{10}$  V.S. of  $\text{AgNO}_3$  for complete precipitation?

4. How much pure NaBr is contained in a sodium bromide of which 1 Gm dissolved in water requires 10 ml of  $\frac{N}{10}$  V.S. of  $\text{AgNO}_3$  for complete precipitation?

5. How much pure KI is contained in a solution of which 2 Gm requires 12 ml  $\frac{N}{10}$  V.S. of  $\text{AgNO}_3$  for complete precipitation?

6. How much pure KBr is contained in a solution of which 2 Gm requires 12 ml  $\frac{N}{10}$  V.S. of  $\text{AgNO}_3$  for complete precipitation?

7. How much pure KCl is contained in a solution of which 2 Gm requires 12 ml of  $\frac{N}{10}$  V.S. of  $\text{AgNO}_3$  for complete precipitation?

8. How much  $\frac{N}{10}$  V.S. of  $\text{AgNO}_3$  is required to completely precipitate a solution of 1 Gm KI? 1 Gm KBr? 1 Gm KCl?

9. How much  $\frac{N}{10}$  V.S. of  $\text{AgNO}_3$  is required to completely precipitate a solution of 1 Gm of a potassium iodide sold as pure but which consists of 90 per cent KI and 10 per cent KBr?

10. How much  $\frac{N}{10}$  V.S. of  $\text{AgNO}_3$  is required for the complete precipitation of 5 Gm of a solution containing 20 per cent of a mixture consisting of 50% KI, 20% KBr and 30% KCl?

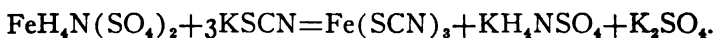
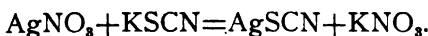
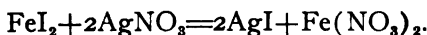
**840. Decinormal V.S. of potassium sulphocyanate.**

$\text{KSCN} \equiv 97$ . Each ml contains 0.0097 Gm

This solution may be used to cause the complete precipitation of silver from solutions of silver salts, and as a delicate test for ferric salts with which it produces a blood-red or reddish-brown color.

How much ferrous iodide is contained in a syrup of iodide of iron tested as follows: 3 Gm of the syrup is mixed with 20 ml of water, 21 ml of  $\frac{N}{10}$  V.S. of  $\text{AgNO}_3$ , then 10 ml of dilute nitric acid and 10 ml of T.S. of iron alum; the liquid is then found to require 2 ml of  $\frac{N}{10}$  V.S. of KSCN to produce a reddish-brown color which is not discharged on shaking.

The reactions are as follows:



[The quantity of V.S. of  $\text{AgNO}_3$  used is an excess. The quantity actually required to form AgI is then found by precipitating the surplus silver salt by KSCN, which is carefully added until a permanent reddish-brown coloration (from ferric sulphocyanate) is produced.]

anate) is produced with the iron alum which is added simply to act as an indicator.

THE USE OF OXIDIZING AGENTS AND REDUCING AGENTS IN VOLUMETRIC ANALYSIS.

**841.** The oxidizing agents used are bromine, iodine, potassium permanganate, and potassium dichromate; the reducing agents are oxalic acid and sodium thiosulphate. The customary method of expressing the measure of the power of oxidizing agents is to refer to the number of oxygen atoms assumed to be liberated and thus rendered available for effecting the oxidation of other substances; and the power of reducing agents is usually also expressed with reference to the number of oxygen atoms they can take, or their equivalent.

But these methods of expression are not clear and direct. It is better to measure the power of oxidizing agents in units of atomic polarity-value lost by each molecule, and the power of reducing agents in units of atomic polarity-value gained by each molecule.

**842.** We are told that "two molecules of potassium permanganate,  $2\text{KMnO}_4=316$ , in oxidation, give off, in the presence of acids, five atoms of O, which are equivalent to ten atoms of H; hence its normal solution should contain  $\frac{316}{10}$  or 31.6 Gm in 1 liter." To illustrate how two molecules of  $\text{KMnO}_4$  give off five atoms of O, the following equation is generally presented:

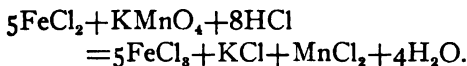
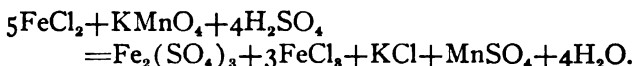
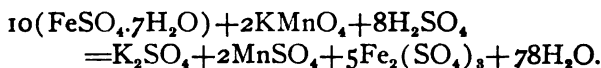
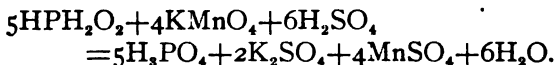
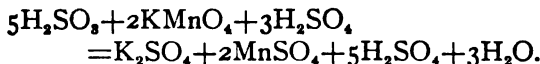
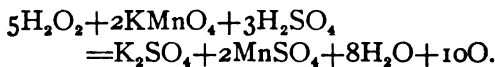


This equation is, however, only theoretically correct; it never occurs. Oxygen is not liberated from  $\text{KMnO}_4$  by dilute  $\text{H}_2\text{SO}_4$ ; the two substances do not react without the aid of a third substance acting as a reducing agent.

We prefer, therefore, to say that each molecule of  $\text{KMnO}_4$  in oxidation gives up five units of polarity-value from its manganese atom, and that for this reason we would make a normal volumetric solution of it containing  $\frac{158}{5}$  Gm in each liter, the mol. w. of the salt being 158.

The following equations represent actual reactions showing the number of units of polarity-value transferred by  $\text{KMnO}_4$ , as

an oxidizing agent, to the respective reducing agents participating in the interactions.



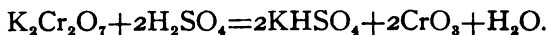
All of these equations show that the Mn of each molecule of  $\text{KMnO}_4$  in which it has a polarity-value of +7 reappears in the  $\text{MnSO}_4$  with a polarity-value of +2. It, therefore, lost 5 units. Consequently, in the reaction represented by the third equation, the two molecules of  $\text{KMnO}_4$  together lost 10 units, all of which were taken by the carbon atoms, for the algebraic sum of the units of polarity-value of the 10 carbon atoms in the two molecules of oxalic acid is 30, whereas the algebraic sum of the carbon atoms of the  $10\text{CO}_2$  is 40.

**843.** We are told that potassium dichromate when employed as an oxidizing agent "gives off, from each molecule, three atoms of oxygen available for oxidation," and this is usually illustrated by the following theoretical equation:



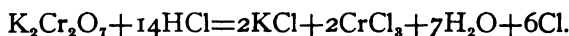
But such a reaction as is represented by this equation never takes place; potassium dichromate and sulphuric react with each

other not to form chrome alum and oxygen, but to form acid potassium sulphate and chromic anhydride, as follows:

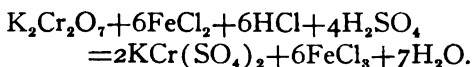
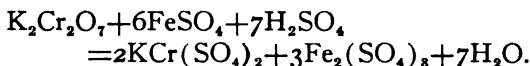
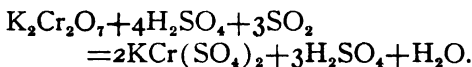


In this reaction there is no oxidation at all.

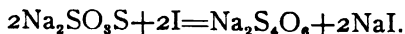
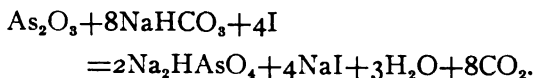
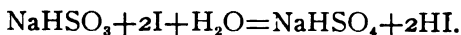
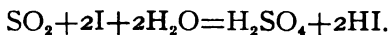
But the oxidizing action of  $\text{K}_2\text{Cr}_2\text{O}_7$  is clearly shown in the following reactions:



(Heat is necessary to cause the foregoing reaction.)



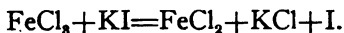
**844.** Reactions of iodine and of sodium thiosulphate occur as follows:



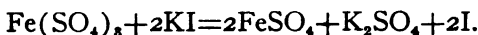
**845.** The iodometric method of determination of the value of ferric salts and their solutions depends primarily upon the prompt liberation of iodine in the solutions to be tested and the sharpness of the reaction between that iodine and the sodium thiosulphate employed. Ferric iodide is extremely unstable. In fact, it may be said not to exist in *water-solution*. Hence whenever

potassium iodide is added to the solution of any ferric salt, ferric iodide is not formed, but the ferric salt is reduced to ferrous, the potassium of the KI taking up one-third of the negative radical of the ferric salt, and the iodine is set free.

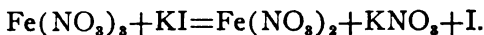
With ferric chloride the reaction is as follows:



With ferric sulphate:

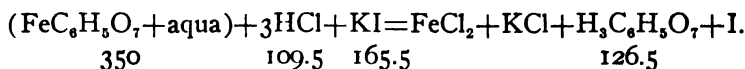
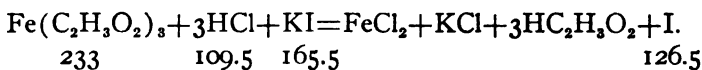
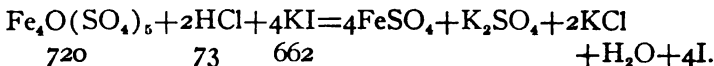
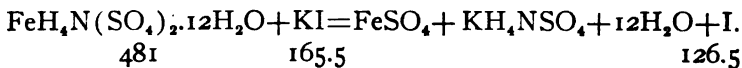
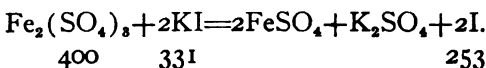
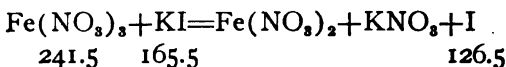
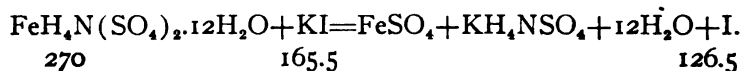


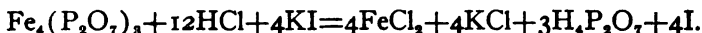
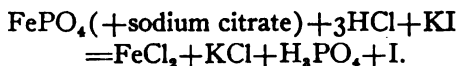
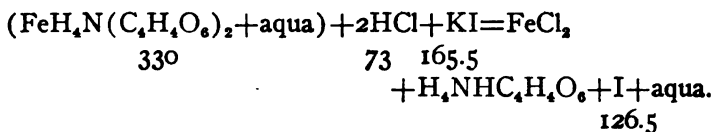
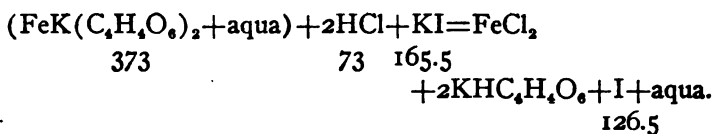
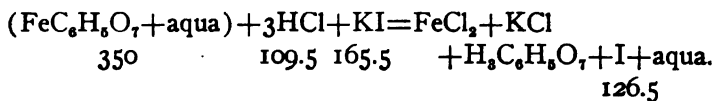
With ferric nitrate:



But potassium iodide does not react with the ferric scale salts and with certain other ferric compounds except in the presence of hydrochloric acid, sulphuric acid, or some other suitable acid.

The following equations show the reactions which take place in the iodometric method of valuation of official ferric compounds:





**846.** As will be seen from the foregoing equations each iron atom contained in any one of the ferric compounds suffers a reduction of its polarity-value amounting to 1 unit, and this unit of polarity-value releases 1 atom of iodine from the KI. When the V.S. of sodium thiosulphate is then added the quantity of free iodine contained in the liquid is determined by the formation of NaI and Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub>, both of which are colorless and do not produce a blue color with starch mucilage. As long as any free iodine remains in the liquid the latter (or the starch in it) is blue, but when all of the iodine has been consumed in the formation of NaI, the blue color is at once discharged, and the quantity of V.S. of Na<sub>2</sub>SO<sub>3</sub>S required to cause the discharge of the blue color, therefore, indicates the exact amount of free iodine which was contained in the liquid, and as each atom of iodine was set free by the reduction of one atom of iron every milliliter of V.S. of Na<sub>2</sub>SO<sub>3</sub>S consumed registers the presence of 0.0056 Gm of iron in the ferric compound tested.

**847.** The Pharmacopœia prescribes the same quantities of hydrochloric acid and potassium iodide in all these tests, namely, 2 ml of the official acid and 1 Gm of KI for 0.56 Gm of any ferric compound or for 1.12 Gm of the solution of any ferric

compound. These quantities are far in excess of the amounts required according to the chemical equations; but the excess of either HCl or KI or both can not interfere with or vitiate the result.

In the solution of the problems here presented it is understood that the right quantities of water, hydrochloric acid and potassium iodide have been added to the test sample, that the reaction whereby the iodine is set free has been completed by heating the mixture for half an hour at about  $40^{\circ}$ , and that enough starch T.S. has been added to the cooled mixture. It is, therefore, unnecessary to consider any other factors in the stoichiometric calculations except the quantity (Gm) taken of the ferric preparation and the quantity (ml) required of the  $\frac{N}{10}$  V.S. of  $\text{Na}_2\text{SO}_3\text{S}$ , each ml of which corresponds to or indicates 0.0056 Gm of iron.

**848.** As the atomic weight of iron is 56 it follows that when the molecular weight of any iron compound containing one iron atom is multiplied by the percentage of iron it contains the product must be 5600; when one-half of the mol. w. of an iron compound containing 2 iron atoms is multiplied by the percentage of iron in that compound the product is also 5600; and the same product is obtained when the percentage of iron is multiplied by one-third of the mol. w. of any iron compound containing 3 atoms of Fe, or with one-fourth of the mol. w. of any iron compound containing 4 iron atoms in each molecule.

This may be readily seen from the following examples:

As the mol. w. of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  is 270 and each molecule contains one iron atom ( $\text{Fe}=56$ ) and the iron contained in it accordingly amounts to 20.74 per cent we have  $270 \times 20.74 = 56 \times 100$ .

Crystallized iron alum,  $\text{FeH}_4\text{N}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , contains 11.6 per cent of iron; its mol. w. is 482. Hence  $482 \times 11.6 = 56 \times 100$ .

Many of the ferric compounds of the Pharmacopœia contain more or less water, and this is necessarily taken into account in the official methods of volumetric assay. The known or assumed (or permitted) proportion of water being added to the molecular weight, we shall have:

1. Ferric chloride:  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + \text{moisture} = 280$ . It then contains 20% of iron or 56 parts in 280. Hence  $280 \times 20 = 56 \times 100$ .

2. Ferric citrate,  $\text{FeC}_6\text{H}_5\text{O}_7 + \text{aqua} = 350$ , contains 16% of iron. Hence  $350 \times 16 = 56 \times 100$ .

Citrate of iron and ammonium and citrate of iron and strychnine also contain 16% of iron.

3. Citrate of iron and quinine, including the quinine and moisture, is assumed to contain 56 parts of iron in 386 parts, or 14.5 per cent, for  $386 \times 14.5 = 56 \times 100$ .

4. Iron and potassium tartrate contains 56 parts of iron in about 373 parts, or 15%, for  $373 \times 15 = 56 \times 100$ .

5. Iron and ammonium tartrate contains 56 parts of iron in about 330 parts, or 17%, for  $330 \times 17 = 56 \times 100$ .

6. Soluble ferric phosphate contains 56 parts of iron in about 467 parts, or 12%, as  $467 \times 12 = 56 \times 100$ .

7. Soluble pyrophosphate of iron contains 56 parts of iron in about 560 parts, or 10%, for  $560 \times 10 = 56 \times 100$ .

When solutions of ferric compounds are considered, the same principle is applied—the weight of the water must be added to the weight of the iron compound. Hence:

8. Solution of ferric chloride containing 37.8% of  $\text{FeCl}_3 = 162$  must, therefore, contain 56 parts of iron in 431 parts of the solution (equal to 162 parts of  $\text{FeCl}_3$ ), or 13%.

$$431 \times 13 = 56 \times 100.$$

9. A solution of ferric nitrate containing 6.2% of  $\text{Fe}(\text{NO}_3)_3 = 241.5$ , must contain 56 parts of iron in 4000 parts of the solution, or 1.4% [4000 parts of solution of 6.2% strength would equal 241.5 parts of  $\text{Fe}(\text{NO}_3)_3$ ].

$$4000 \times 1.4 = 56 \times 100.$$

10. A solution of ferric sulphate containing 28.7% of  $\text{Fe}_2(\text{SO}_4)_3 = 400$ , must contain 56 parts of iron in 700 parts of the solution (equal to 200 parts of the salt), or 8%.

$$700 \times 8 = 56 \times 100.$$

11. A solution of subsulphate of iron containing 43.7% of  $\text{Fe}_4\text{O}(\text{SO}_4)_6 = 720$ , must contain 56 parts of iron in 412 parts of the solution (equal to 180 parts of salt), or 13.6%.

$$412 \times 13.6 = 56 \times 100.$$

12. A solution of ferric acetate which contains 31% of

$\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$  must contain 56 parts of iron in about 750 parts of the solution, or about 7.5 per cent.

$$750 \times 7.5 = 56 \times 100.$$

13. A solution of ferric citrate yielding about 44 per cent of scales and containing about 56 parts of iron in about 750 parts therefore contains about 7.5% of iron.

$$750 \times 7.5 = 56 \times 100.$$

849. It is evident from the foregoing statements that the number of grams of the ferric preparation corresponding to 56 Gm of iron must require 10,000 ml of the V.S. of  $\text{Na}_2\text{SO}_3\text{S}$  since each ml of that solution indicates 0.01265 Gm of iodine or 0.0056 Gm of iron. It is equally clear that 56 Gm of the ferric preparation must require 10,000 ml. of the V.S. of  $\text{Na}_2\text{SO}_3\text{S}$  multiplied by the proportion of iron contained in the preparation tested. For example, since about 350 Gm of scaled citrate of iron contains about 56 Gm of iron, a solution containing 350 Gm of that ferric citrate would (after adding the HCl and KI and starch solution) require 10,000 ml of V.S. of  $\text{Na}_2\text{SO}_3\text{S}$ , and as 56 is 16% of 350 it follows that 56 Gm of ferric citrate would require 16 per cent of 10,000 ml of the volumetric solution, or 1600 ml, and that 0.56 Gm would require 16 ml. It is further evident that each ml of V.S. of  $\text{Na}_2\text{SO}_3\text{S}$  must accordingly indicate 1 per cent of iron in the ferric preparation tested, since  $350 \times 16 = 56 \times 100$  and each ml of the V.S. indicates 0.0056 Gm of iron.

For this reason the Pharmacopœia prescribes that 0.56 Gm of the ferric preparation be taken to perform the volumetric assay, so that the number of ml of V.S. of  $\text{Na}_2\text{SO}_3\text{S}$  required at once indicates the per cent of iron contained in the preparation. Whenever 1.12 Gm (or twice 0.56 Gm) is taken the number of ml of V.S. of  $\text{Na}_2\text{SO}_3\text{S}$  required must, of course, be twice as great, so that each ml of V.S. of  $\text{Na}_2\text{SO}_3\text{S}$  then indicates only 0.5 per cent; but the Pharmacopœia orders 1.12 Gm to be taken of any *solution* of a ferric compound, because 1.12 Gm of a liquid can be weighed more accurately than 0.56 Gm, and because some of these solutions contain a comparatively small per cent of iron (the solution of ferric nitrate contains only 1.4% of iron, which would require only 1.4 ml of V.S of  $\text{Na}_2\text{SO}_3\text{S}$  if only 0.56 Gm of the preparation were taken for the test).

**850. Decinormal V.S. of iodine.**

$I=126.5$ . Each ml  $=0.01265$  Gm

Free iodine as used in iodometric determinations acts as an oxidizing agent, because the iodine used forms an iodide and thus changes its polarity-value from 0 to  $-1$ . The solution of iodine is made with the aid of KI, but the KI can not interfere with the reaction. It will be seen that the decinormal V.S. of iodine contains 12.65 Gm of iodine in each liter—not because “the molecular weight divided by the valence” requires that a “normal solution” of iodine should contain 126.5 Gm (the mol. w. of I is, in fact,  $126.5 \times 2$  or more at any temperature below  $600^\circ$ ; but because one atom of iodine, employed as an oxidizing agent, supplies one unit of polarity-value.

1. How much sodium thiosulphate ( $Na_2SO_3 \cdot 5H_2O=248$ ) will be required to completely decolorize 10 ml of  $\frac{N}{10}$  V.S. of iodine?

And how much  $\frac{N}{10}$  V.S. of iodine must be added to a solution containing 0.25 Gm of sodium thiosulphate to produce a permanent iodine reaction on starch? And why?

2. How much  $H_2SO_3$  is contained in a solution 1 Gm of which requires 20 ml of  $\frac{N}{10}$  V.S. of iodine to impart a permanent blue color to the starch (a few drops of starch mucilage being first added to the solution of  $H_2SO_3$ )?

3. How much  $\frac{N}{10}$  V.S. of iodine is decolorized by a solution prepared from 0.2 Gm  $As_2O_3$  and 2 Gm of  $NaHCO_3$ ?

4. What per cent of  $H_2HAsO_3$  is contained in a solution 25 Gm of which (after having been boiled for a few minutes with 2 Gm of  $NaHCO_3$ ) decolorizes 50 ml of  $\frac{N}{10}$  V.S. of iodine? And why?

5. How much  $Na_2SO_3 \cdot 7H_2O$  will be required to decolorize 25 ml of  $\frac{N}{10}$  V.S. of iodine? And why?

6. If a solution be made of 0.3235 Gm of dry  $KSbOC_4H_4O_6$ , 10 Gm of water, and 20 ml of a cold saturated solution of  $NaHCO_3$ , and a few drops of T.S. of starch added, how much  $\frac{N}{10}$  V.S. of iodine will be required to produce a permanent blue color in the mixture? And why?

**851. Decinormal V.S. of sodium thiosulphate.**

$Na_2SO_3 \cdot 5H_2O=248$ . Each ml  $=0.0248$  Gm

This solution is a reducing agent. Each molecule of  $\text{Na}_2\text{SO}_3\text{S}$  takes up one unit of oxidation in forming  $\text{Na}_2\text{S}_4\text{O}_6$ .

One molecule of sodium thiosulphate offsets one atom of iodine. Hence 1 ml of decinormal sodium thiosulphate solution, containing 0.0248 Gm of the salt, decolorizes 1 ml of decinormal iodine solution, containing 0.01265 Gm of iodine.

1. What per cent of iodine is contained in a solution 12.65 Gm of which requires 30 ml of  $\frac{N}{10}$  V.S. of sodium thiosulphate? And why?

2. For testing tincture of iodine the Pharmacopœia orders 2 Gm of KI and 25 Gm of water to be added to 6.3 ml of the official tincture, and the addition of a little T.S. of starch. This mixture should then require about 35 ml of  $\frac{N}{10}$  V.S. of sodium thiosulphate.

What *per cent* of iodine does this indicate?

Why is the KI added?

Why is the starch added?

3. A water-solution of chlorine is to be tested to determine the per cent of chlorine it contains. If 71 Gm of this solution be added to another solution made of 4 Gm of KI and 40 Gm of water, the mixture becomes deep-red; why? If 28.75 Gm of this mixture requires 25 ml of  $\frac{N}{10}$  V.S. of sodium thiosulphate to be completely decolorized, what per cent of chlorine is contained in the solution? And why? Why is the KI added?

4. If 0.30 Gm. of chlorinated lime be well triturated with 50 Gm of water and the solution together with the washings transferred to a flask, then 0.75 Gm of KI added, and finally 5 Gm of diluted hydrochloric acid; and if this mixture require 30 ml  $\frac{N}{10}$  V.S. of sodium thiosulphate for complete decoloration, what is the per cent of chlorine in that chlorinated lime? And why?

5. If 2.8 Gm of crystalline ferric chloride be dissolved in water and subjected to the iodometric method of determination of the amount of iron in it, how many ml of V.S. of  $\text{Na}_2\text{SO}_3\text{S}$  will be consumed if the sample be pure  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ?

And what per cent of Fe will be indicated by each ml of the V.S.

6. If 2.8 Gm of a solution of ferric chloride be subjected to the iodometric method of assay and it should be found that 25 ml of V.S. of  $\text{Na}_2\text{SO}_3\text{S}$  is required to consume the free iodine, then what per cent of  $\text{FeCl}_3$  is contained in the solution tested?

What per cent of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  is contained in it?

And what per cent of Fe?

And what per cent of Fe is in this case indicated by each ml consumed of the V.S.?

7. I dissolve 1 Gm of citrate of iron in water, add HCl and KI, digest half an hour, cool, add a few drops of T.S. of starch, and then add V.S. of  $\text{Na}_2\text{SO}_3\text{S}$ . How many ml of the V.S. will be required to discharge the blue color if the ferric citrate contain 16 per cent of Fe?

8. If 1.12 Gm of soluble ferric pyrophosphate be tested by the iodometric method how many ml of V.S. of  $\text{Na}_2\text{SO}_3\text{S}$  will be consumed, assuming that the preparation contain 10 per cent of Fe?

9. If 2.24 Gm of solution of ferric acetate be assayed by the iodometric method to determine the per cent of iron in it, and 20 ml of V.S. of  $\text{Na}_2\text{SO}_3\text{S}$  should be required to consume the free iodine, what per cent of Fe would that indicate?

10. If 20 ml of V.S. of  $\text{Na}_2\text{SO}_3\text{S}$  be required to consume the iodine liberated by 1 Gm of solution of ferric chloride, what is the per cent of Fe in the preparation? What the per cent of  $\text{FeCl}_3$ ? And what the per cent of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ?

11. If 2.24 Gm of solution of ferric citrate tested by the iodometric method should require 30 ml of V.S. of  $\text{Na}_2\text{SO}_3\text{S}$ , how many Gm of Fe would be contained in 100 Gm of that solution?

12. If 4 Gm of solution of ferric nitrate should liberate enough iodine to require 10 ml of V.S. of  $\text{Na}_2\text{SO}_3\text{S}$  for the discharge of the blue color produced upon starch by that iodine, what would be the per cent of ferric nitrate contained in the solution tested? And what the per cent of Fe?

13. How many Gm of  $\text{Fe}(\text{OH})_3$  can be prepared out of 1000 Gm of a solution of  $\text{Fe}_2(\text{SO}_4)_3$  of which 1 Gm liberates from KI a quantity of iodine which consumes  $17.8 \text{ ml of } \frac{N}{10}$  V.S. of  $\text{Na}_2\text{SO}_3\text{S}$  to discharge the iodine reaction on starch?

### 852. Decinormal V.S. of potassium dichromate.

$\text{K}_2\text{Cr}_2\text{O}_7 = 294$ . Each ml contains 0.0049 Gm

As the two chromium atoms of one molecule of  $\text{K}_2\text{Cr}_2\text{O}_7$  possess together 12 units of polarity-value, and as 6 of these units are transferred by it to the reducing agent with which it is used in

volumetric analysis, it follows that in order to make a *normal* solution of  $K_2Cr_2O_7$  we must take for each liter  $\frac{294}{6}$  Gm, or 49 Gm, and for a *decinormal* solution  $\frac{294}{60}$  Gm, or  $\frac{49}{10}$  Gm, of the salt.

When  $K_2Cr_2O_7$  is used as an oxidizing agent *in the presence of sulphuric acid* it forms chrome alum,  $KCr(SO_4)_2$ . In the presence of hydrochloric acid it forms  $CrCl_3$ .

How much  $\frac{N}{10}$  V.S. of  $K_2Cr_2O_7$  will be required to convert 1.39 Gm of crystallized ferrous sulphate,  $FeH_2SO_4 \cdot 6H_2O$ , into ferric sulphate,  $Fe_2(SO_4)_3$ ?

### 853. Decinormal V.S. of potassium permanganate.

$KMnO_4 = 158$ . Each ml contains 0.00316 Gm

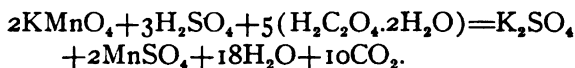
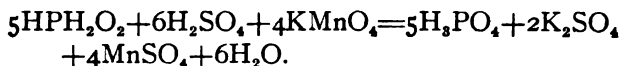
As the polarity-value of the Mn in the  $KMnO_4$  is +7, and as it forms a manganous salt in the presence of a strong acid together with a reducing agent (the Mn changing its functions from acidic to basic by reason of the predisposing affinity of the manganous base for the sulphuric or other acid present), the student will see that the Mn suffers a reduction of its polarity-value from +7 to +2. Hence to make a *normal* solution we take for each liter  $\frac{158}{5}$  Gm of  $KMnO_4$ , and for a decinormal solution we must take  $\frac{158}{50}$  Gm of this oxidizing agent.

1. I have a solution containing an unknown quantity of oxalic acid in water. I find that 2 Gm of the solution, acidulated with sulphuric acid, will decolorize 10 ml of  $\frac{N}{10}$  V.S. of  $KMnO_4$ . What per cent of  $H_2C_2O_4$  does the solution contain? And what per cent of  $H_2C_2O_4 \cdot 2H_2O$ ?

2. If 5 ml of solution of hydrogen dioxide properly diluted, and acidulated with a sufficient quantity of diluted sulphuric acid, decolorizes 30 ml of  $\frac{N}{10}$  V.S. of  $KMnO_4$ , what per cent of  $H_2O_2$  is contained in the solution tested?

3. 1 Gm of a diluted hypophosphorous acid is mixed with 14 ml of sulphuric acid and 70 ml of  $\frac{N}{10}$  V.S. of  $KMnO_4$  and the mixture boiled for fifteen minutes. It then requires 10 ml of  $\frac{N}{10}$  V.S. of oxalic acid to discharge the red color. How many per cent of  $HPH_2O_2$  does that acid contain?

The reactions are:



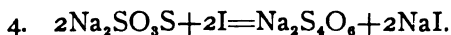
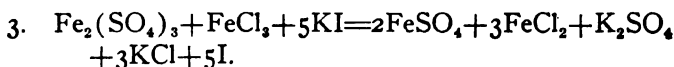
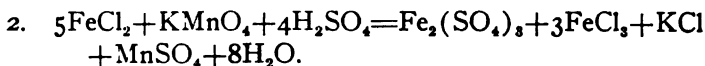
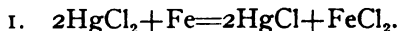
[The  $\text{KMnO}_4$  is first added in excess. Subsequently the exact excess is determined by titration with oxalic acid. The decinormal solutions cancel each other, volume for volume.]

4. I have a solution of ferrous sulphate of unknown strength. I find that 10 Gm of it, acidulated with  $\text{H}_2\text{SO}_4$ , requires 30 ml of  $\frac{N}{10}$  V.S. of  $\text{KMnO}_4$  to produce a permanent pink color. How many per cent of  $\text{FeH}_2\text{SO}_5$  does the solution contain? What per cent of crystallized ferrous sulphate does it correspond to? What per cent of Fe does it contain?

5. I put 1 Gm of "reduced iron" and 100 ml of a five per cent solution of  $\text{HgCl}_2$  in a bottle, digest over a water-bath for an hour, shaking often, and then let cool. Then add 200 ml water, and filter. I mix 10 ml of the filtrate with an equal volume of diluted sulphuric acid, and then add enough  $\frac{N}{10}$  V.S. of  $\text{KMnO}_4$  to produce a permanent pink color, and find that 9 ml of the V.S. is required. What is the per cent of Fe contained in the sample tested?

I now add a few drops of alcohol to decolorize the liquid and then 1 Gm of KI, after which I let the mixture digest for half an hour at  $40^\circ$ , and then let it cool and add some drops of T.S. of starch. How much  $\frac{N}{10}$  T.S. of  $\text{Na}_2\text{SO}_3$  will be required to discharge the color, assuming that the preceding assay gave a correct result?

The reactions are:





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